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THE MASS YIELD CURVE FOR FISSION OF Am^{241} BY PILE NEUTRONS

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Abstract—Relative yields for the fission of Am^{241} by pile neutrons have been measured for mass numbers 89, 91, 95, 97, 99, 111, 113, 115, 121, 131, 132, 136, (shielded), 137, 139, 140, 141, 143, 144, 147 and 153. The peak-to-trough ratio is ~160 and $\bar{\nu}$ is 3 ± 0·5. The light peak has moved two mass units towards the heavy peak when compared with the Pu^{239} thermal fission curve.

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WHILE fission yield data for the thermal fission of U^{233}, U^{235} and Pu^{239} are fairly plentiful, only two papers have so far been published for fission of nuclides of higher mass. These are for the spontaneous fission of Cm^{242} [1] and Cf^{252}.[2] No other fission data are available for nuclides of higher mass than Pu^{239}. In addition to the higher mass, the "fissionability parameter," Z^2/A for Am^{241} is higher than that for any of the thermally fissile nuclides previously used for fission yield measurements.

This paper gives the relative fission yields for nineteen mass chains for the pile neutron fission of Am^{241}. In addition, the yield of one shielded nuclide is reported.

EXPERIMENTAL

Purification of the americium

The americium received had been obtained by removing it from a source of plutonium which contained a high proportion of Pu^{241}. Since the americium which had grown in had been removed from this same plutonium source twice previously, any Am^{242} which was originally present owing to $(n\gamma)$ reactions in the pile could now be assumed to be entirely removed. It was heavily contaminated with plutonium, from which it was separated by passing it seven times through anion exchange columns (a fresh column for each run) as a solution in concentrated hydrochloric acid containing ~1% of nitric acid. This procedure is known to produce pure americium from plutonium. The purified americium was precipitated with ammonia and dissolved in 0·5 N nitric acid. As an additional check on the purity, an aliquot of the final solution was examined by α-pulse analysis and no α-emitter other than Am^{241} could be detected.

Irradiations

A calculation was made to find out at what point growth of Am^{242} and Am^{242m} formed by neutron capture in the Am^{241} would be sufficient for the fission of these to contribute significantly to the total fission. The calculation showed that after ten hours irradiation in Bepo in a flux of 10^{12} n/cm²/sec the number of fissions occurring due to Am^{242} and Am^{242m} together would have risen to ~1% of the fissions occurring due to Am^{241}, and ten hours was therefore fixed as the maximum total irradiation to which any sample of the americium would be subjected.

The majority of the irradiations were carried out in the pneumatic tube of Bepo, but the isotope belt stringer was used for a few of the longer ones. The neutron flux in these positions is approximately 85% thermal and 15% fast neutrons, where "thermal" is taken to mean those neutrons in a Maxwellian distribution up to ~0·3 eV and "fast" is taken to mean those above 0·3 eV. The ratio of neutrons of energies >1 MeV to those of energies <1 MeV is ~1 : 75. Since the thermal and

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[1] E. P. STEINBERG and L. E. GLENDENIN *Phys. Rev.* **95**, 431 (1954).
[2] L. E. GLENDENIN and E. P. STEINBERG *J. Inorg. Nucl. Chem.* **1**, 45 (1955).

fast-neutron fission cross-sections are probably about the same, the fission yield curve presented is probably for about 85% thermal and 15% fast fissions but it is impossible to be certain of this in the present state of our knowledge. The length of the irradiations varied from thirty minutes to eight hours.

For most of the irradiations a sample of the americium weighing between 0·1 and 1 mg was pipetted into a silica capsule, evaporated to dryness and sealed off. The capsule was cut open after the irradiation and the pieces immersed in an acid solution of the appropriate carriers and heated to dissolve the americium and fission products. In order to check that this procedure did not introduce any errors because of selective dissolution of fission fragments embedded in the walls of the silica capsule, a few irradiations were carried out in thin pure aluminium containers which were sealed by cold welding. The entire container was dissolved in the acid carrier solution after irradiation. No significant differences in the ratios of Sr^{89}, Y^{91}, Zr^{95}, Mo^{99} or Cd^{115} to Ba^{140} were found in these runs as compared with those carried out in silica.

Chemical separations and purifications

After dissolving the irradiated americium in a glove box, the elements whose fission yields were being measured were separated from the americium and removed from the box for purification. Barium was separated in every case to act as a reference source. Individual elements were treated as follows.

Strontium

Americium was removed by a ferric iron scavenge, and barium and strontium were then precipitated as carbonates. Strontium was purified by barium scavenges, nitrate precipitation, chromate precipitation and final precipitation as sulphate.

Yttrium and rare earths

These elements were purified by cation exchange as described by CUNINGHAME *et al.*[3] Some cerium samples were separated and purified by the method of GLENDENIN *et al.*[4] Rare earths were mounted as oxalate.

Zirconium

This was purified by a series of hydroxide precipitations followed by mandelic acid precipitations and mounted as mandelate.

Molybdenum

The americium was removed by a ferric iron scavenge and the molybdenum purified by α-benzoin oxime purifications and mounted as 8-hydroquinolate.

Silver

The americium was removed by a ferric iron scavenge and the silver purified by the method of GLENDENIN,[5] and mounted as silver chloride.

Cadmium

The americium was removed by a ferric iron scavenge and the cadmium purified by a combination of sulphide precipitations and ferric scavenges and mounted as 8-hydroxyquinolate.

Tin

The americium was removed by a ferric iron scavenge using sodium hydroxide to keep the tin in solution. The tin was purified by the method of NEWTON[6] and mounted as tin dioxide.

[3] J. G. CUNINGHAME, M. L. SIZELAND, H. H. WILLIS, J. EAKINS, and E. R. MERCER *J. Inorg. Nucl. Chem.* **1**, 163 (1955).
[4] L. E. GLENDENIN, K. F. FLYNN, R. F. BUCHANAN, and E. P. STEINBERG *Anal. Chem.* **27**, 59 (1955).
[5] L. E. GLENDENIN National Nuclear Energy Series, Vol. 9B Paper 2672 McGraw-Hill, New York, 1953.
[6] A. S. NEWTON *Phys. Rev.* **75**, 17 (1949).

Tellurium

The carrier was evaporated three times to dryness with hydrobromic acid and then dissolved in concentrated hydrochloric acid and diluted to 3 N. Tellurium metal was precipitated with sodium bisulphite and purified by the method of GOECKERMANN as quoted by MEINKE.[7] The tellurium was mounted as the element.

Iodine

Iodide carrier was warmed in dilute hydrochloric acid solution before being made alkaline with sodium hydroxide. The iodine was oxidized with sodium hypochlorite before removal of the precipitated americium. The iodine was purified by repeated carbon tetrachloride extraction cycles and mounted as silver iodide.

Caesium

The americium was removed by a ferric iron scavenge and the caesium purified by the method of BARTHOLOMEW and BAERG.[8]

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Barium

The americium was removed by a ferric iron scavenge and the barium precipitated as carbonate or sulphate. It was purified by nitrate and chloride precipitations and a final ferric iron scavenge and mounted as the sulphate.

Counting procedures

The purified sources were filtered by a filter-stick technique. This gave very smooth and even precipitates 1·6 cm in diameter and of weight usually about 20 mg, mounted on filter papers fixed to a thick aluminium tray. Chemical yields were obtained by direct weighing.

Counting corrections were applied for self-absorption, self-scattering and back-scattering from source and tray, and for conversion electrons, growth of daughter nuclides and other genetic phenomena. For Sr^{89}, Y^{91}, Zr^{95}, Zr^{97}, Mo^{99}, Ag^{111}, Cd^{115}, Ba^{140}, Ce^{141}, Pr^{149}, Nd^{147} and Sm^{153}, the details of these corrections appear in a report by CUNINGHAME, SIZELAND and WILLIS.[9] Corrections for Ag^{113}, Sn^{121}, I^{131}, Te^{132}, Cs^{137} and Ba^{139} have been measured by the same authors and will appear shortly as an A.E.R.E. report.[10] The corrections for Cs^{136} were estimated by comparison with corrections for nuclides of similar maximum β energy.

All sources except very long-lived ones were counted for at least five half-lives to check radiochemical purity.

Calculations

Saturation activities were computed for all samples, normal growth and decay relationships being used, and independent yields being assumed to be negligible. Where the parent of the nuclide concerned was of significant half-life the following expression was used to calculate the saturation activity.

$$A_s = A_0/f$$

where A_s = saturation activity

A_0 = observed activity at time t

and

$$f = \frac{\lambda_2}{\lambda_2 - \lambda_1}\left[e^{-\lambda_1 t}(1 - e^{-\lambda_1 T}) - e^{-\lambda_2 t}(1 - e^{-\lambda_2 T})\right] + e^{-\lambda_2 t}(1 - e^{-\lambda_2 t})$$

where λ_1 and λ_2 are the parent and daughter decay constants respectively,

t is the time elapsed between the end of the irradiation and the separation of parent and daughter,

T is the irradiation time.

[7] W. W. MEINKE U.S.A.E.C. Report AECD 2738 (1949).
[8] R. M. BARTHOLOMEW and A. P. BAERG *Canad. J. Chem.* 34, 201 (1956).
[9] J. G. CUNINGHAME, M. L. SIZELAND, and H. H. WILLIS A.E.R.E. C/R 1646 (1955).
[10] J. G. CUNINGHAME, M. L. SIZELAND, and H. H. WILLIS A.E.R.E. C/R 2054: to be issued.

The standard deviations quoted in the results were calculated for each nuclide separately by estimating the spread of every possible error and taking the root mean square deviation of all the errors.

Normally at least two results were obtained for each nuclide, but in the case of Pr^{149}, Nd^{147}, and Sm^{153}, only one determination was made and standard deviations have been increased accordingly. Similarly a larger deviation has been applied to Cs^{136} where the counting corrections were estimated instead of measured.

RESULTS

Table 1 gives the fission yields obtained, while Fig. 1 gives the fission yield curve with the Pu^{239} thermal fission curve[11,12] and the Cm^{242} spontaneous fission curve superimposed[1] for comparison. It should be noted that the light peak of the Pu^{239}

TABLE 1.—OBSERVED VALUES OF FISSION YIELDS FOR Am^{241} PILE NEUTRON FISSION

Mass number	Nuclide measured	Fission yield %
89	Sr	0·81 ± 0·05
91	Y	1·16 ± 0·08
95	Zr	3·90 ± 0·51
97	Zr	3·55 ± 0·46
99	Mo	6·85 ± 0·41
111	Ag	0·89 ± 0·05
113	Ag	0·18 ± 0·01
115	54 hr Cd	0·046 ± 0·003
115	43 d Cd	0·004*
115	total	0·050 ± 0·004
121	Sn	0·045 ± 0·006
131	I	3·71 ± 0·19
132	Te	4·48 ± 0·31
136	Cs	0·288 ± 0·032
137	Cs	9·20 ± 1·84
139	Ba	6·22 ± 0·31
140	Ba	6·0 ± 0·36
141	Ce	5·04 ± 0·66
143	Pr	3·32 ± 0·46
144	Ce	3·15 ± 0·41
147	Nd	2·06 ± 0·33
153	Sm	0·76 ± 0·12

* Estimated

curve is made up from the radiochemical results from reference 11, while the heavy peak is from the mass spectrometric results from reference 12. The radiochemical heavy peak results differ radically from the mass spectrometric ones, which have been included solely on the ground that they are newer, without any attempt being made to decide which set is more nearly correct.

The Am^{241} curve has been reflected about mass 119·5, since this gives the best fit to the experimental results. This gives a value of $3 \pm 0{\cdot}5$ for $\bar{\nu}$. It has been drawn so that the area under the curve sums to 200%, giving an absolute value for the fission

[11] E. P. STEINBERG and M. S. FREEDMAN National Nuclear Energy Series, Vol. 9B, Paper 219. McGraw-Hill, New York, 1953.

[12] D. M. WILES, J. A. PETRUSHKA, and R. H. TOMLINSON *Canad. J. Chem.* **34**, 227 (1956).

yield of Ba^{140} of 6·0%. This absolute value is probably accurate to about ±15%. The peak-to-trough ratio is ~160.

DISCUSSION

Shape and position of the peaks

As can be seen from Fig. 1, the light peak in Am^{241} fission has moved approximately two mass units to the right of the Pu^{239} light peak if one considers only the inner

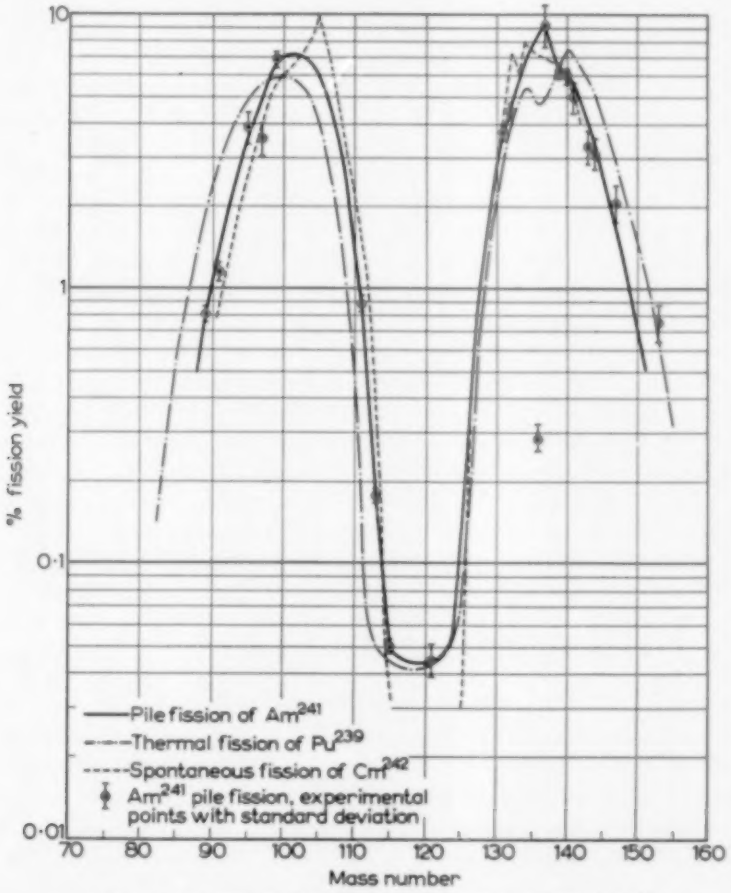

FIG. 1.—The mass-yield curve on the pile neutron fission of Am^{241}.
———Pile fission of Am^{241}
—·—·—Thermal fission of Pu^{239}
– – – – –Spontaneous fission of Cm^{242}
Am^{241} pile fission, experimental points with standard deviation.

edges of the peaks. The Am^{241} peak is, however, taller and narrower than the Pu^{239} peak and shows none of the splaying out of the wings which the latter shows in comparison with the U^{235} thermal fission peak. It will be noted that the Cm^{242} spontaneous fission light peak is even taller and narrower and it is possible that this may account for the fact that the inner edge of this peak is shifted about one mass unit to the right of

the Am^{241} peak, whereas, since the compound nuclei have the same mass, and since $\bar{\nu}$ is the same in both cases, one would expect these peaks to coincide.

The inner edges of all three heavy peaks coincide, but again the Am^{241} peak is taller and narrower than the Pu^{239} peak. There are insufficient data to state definitely that the Cm^{242} peak is narrower still, but from the shape of the curve as far as it goes, it looks as if this is the case.

Peak-to-trough ratio

If the light peak value is taken, this is seen to be $\sim$160. This value is roughly the same as for Pu^{239} and about a factor of 4 smaller than for U^{235} thermal fission. It does not seem advisable to attempt to correlate it with some function of the excitation energy in view of the rather unsatisfactory state of the theory on this point at the present time, and of the fact that the exact proportion of thermal to fast fissions is doubtful.

Fine structure

Insufficient points have been obtained in the mass region 99–111 to determine light peak fine structure. The pronounced fine structure in the heavy peak depends solely on the value found for Cs^{137}, since circumstances did not permit of a determination of Xe^{135} and it was found impossible to get consistent values for Cs^{138}.

Cs^{137} values are not always reliable owing to the possibility of undetected long-lived contamination and to doubts about its half-life. There was insufficient Cs^{137} activity for detailed checks of its radiochemical purity. The half-life used was 28·3 years, which is a mean of the values of BROWN *et al.*[13] and WILES and TOMLINSON[14] and it is unlikely that this value is sufficiently in error to make very much difference to the calculated fission yield. The possibility of long lived contamination cannot be ruled out, although the duplicates (which were entirely separate experiments) agreed to within $4\frac{1}{2}\%$, and the Cs^{136}, which was also found, had the correct half-life. An overall standard deviation of $\pm 20\%$ has been estimated for this nuclide and it is difficult to see how the fission yield can be outside this value, which will still show fine structure at this mass even if the lower limit is used.

The shielded nuclide Cs^{136}

The fractional chain yield is $\sim$0·04 and a value of $(Z - Z_p)$ of 2·0 is calculated from PAPPAS'S theory.[15] With these figures, the Cs^{136} point falls slightly above the smooth curve of $(Z - Z_p)$ against fractional chain yield. It is, however, as nearly on the curve as many of the other points and may be said to be in reasonable agreement with the theory of equal charge displacement.

Zr^{97} and Sm^{153}

The expected values for the yields of both these nuclides seem to be considerably outside the standard deviations estimated from the mass-yield curve. In the case of Sm^{153} the single sample was contaminated with Am^{241}, whose α particles were eliminated by counting through a 10 mg/cm^2 aluminium absorber, and it is possible that the self-absorption correction which had to be estimated is more in error than was

[13] F. BROWN, G. R. HALL, and A. J. WALTER *J. Inorg. Nucl. Chem.* **1**, 241 (1955).
[14] D. M. WILES and R. H. TOMLINSON *Phys. Rev.* **99**, 188 (1955).
[15] A. C. PAPPAS International Conference on the Peaceful Uses of Atomic Energy, Geneva 1955, Paper P/881.

allowed for in the standard deviation. It is also possible that there is some unknown error in this determination but no allowance for such a possibility can be made in estimating the standard deviation.

The case of Zr^{97} is different, since three independent results were within 12% of each other, and there was no contamination. It is worth noting that the Zr^{97} values found for Pu^{239} thermal fission and for Pu^{239} pile neutron fission (11) were also low, and it seems just possible that there is a hitherto undetected short-lived isomer present in Zr^{97} which decays directly to Nb^{97}, or alternatively that the half life of Y^{97} is not negligible, as has been assumed in the calculations.

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DEVIATIONS FROM STRICT HETEROPOLARITY IN CRYSTALLINE HALIDES OF DIVALENT ELEMENTS

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Abstract—Crystal energies of halides of divalent elements derived experimentally by means of the Born-Haber cycle are compared with theoretical values for strict ionic character. The differences between the experimental and theoretical crystal energies can reasonably be correlated with deviations from strict heteropolarity suggested from ionization potentials and anionic polarizabilities.

THE differences in the bond character of simple inorganic crystalline compounds have recently been considered in terms of ionic interaction.[1,2] In the case of crystals regarded as formed through the interaction of cations of the same formal charge and similar (crystal) radius with a common anion, the chemical bonding appears to show greater deviation from strict ionic character the greater the value of the ionization potential of the electropositive constituent (first ionization potential for oxidation number +1, second ionization potential for oxidation number +2, etc.).

A method which has been utilized by SHERMAN[3] and others for indicating deviations from strict heteropolarity in a wide range of crystalline compounds, has been to compare values for the crystal energies obtained from experimental data using the Born-Haber cycle with theoretical values calculated assuming strict ionic character. It is intended here to recalculate and extend SHERMAN's data for the crystal energies of halides of divalent elements, using crystallographic and thermodynamic values from more recent compilations, and to compare the differences Δ between the "experimental" and "theoretical" crystal energies with the second ionization potentials I_2 of the electropositive constituents. A rather similar procedure, but utilizing more refined values for theoretical crystal energies, has been carried out for halides of univalent metals.[1]

For the calculation of experimental crystal energies, SHERMAN used the following equation derived from the Born-Haber cycle;

$$U_{exp} = -\Delta Hf + L + I + D - E \qquad (1)$$

where in the case of a binary uni-univalent crystal the symbols are defined by the following thermochemical equations;

$MX(c) = M^+(g) + X^-(g)$	$\Delta H_{298} = U_{exp}$, crystal energy at 25°C.
$MX(c) = M + \frac{1}{2}X_2$	$\Delta H_{298} = -\Delta Hf$, chemical heat of formation.
$M(c) = M(g)$	$\Delta H_{298} = L$, heat of sublimation.
$\frac{1}{2}X_2 = X(g)$	$\Delta H_{298} = D$, heat of atomization.
$M(g) = M^+(g) + e^-$	$\Delta H_0 = I$, ionization potential.
$X^-(g) = X(g) + e^-$	$\Delta H_0 = E$, electron affinity.

[1] MORRIS D. F. C. and AHRENS L. H. *J. Inorg. Nucl. Chem.* **3**, 263 (1956).
[2] AHRENS L. H. and MORRIS D. F. C. *ibid.* p. 270.
[3] SHERMAN J. *Chem. Rev.* **11**, 93 (1932).

In the calculation of theoretical values, SHERMAN used the Born equation;

$$U_0 = \frac{e^2 z^2 N A_{r0}}{r_0}\left(1 - \frac{1}{n}\right) \tag{2}$$

where U_0 = crystal energy.
e = unit of electrical charge.
z = highest common factor of the oxidation numbers of the ions.
N = Avogadro number.
r_0 = smallest cation-anion distance.
A_{r0} = Madelung constant for use with r_0 values.*
n = Born exponent.

Disadvantages of the Born equation are that it does not take into account van der Waals forces and does not employ an expression for the repulsive potential involving exponential terms in r as required by wave mechanics.[4,5] However, it can be seen from Table 1 that in the case of the halides of sodium, potassium, rubidium, and

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TABLE 1.—CRYSTAL ENERGIES OF ALKALI HALIDES

	(Values in kcal/mole)		
Crystal	Structure type	U_{exp} at 25°C	U_{theo}
NaF	Rock salt	217	217
NaCl	Rock salt	184	182
NaBr	Rock salt	176	173
NaI	Rock salt	165	162
KF	Rock salt	194	192
KCl	Rock salt	170	166
KBr	Rock salt	163	159
KI	Rock salt	154	150
RbF	Rock salt	184	183
RbCl	Rock salt	161	160
RbBr	Rock salt	156	154
RbI	Rock salt	147	145
CsF	Rock salt	172	174
CsCl	Caesium chloride	154	150
CsBr	Caesium chloride	149	145
CsI	Caesium chloride	141	137

U_{theo} values are obtained from U_0 values, calculated with equation (2), by adding the energy due to the pressure-volume products.

U_{exp} values differ slightly from the U values given by MORRIS,[6] as the latter refer to 0°K.

[4] UNSÖLD A. *Z. Physik* **43**, 563 (1927).
[5] PAULING L. *J. Amer. Chem. Soc.* **49**, 765 (1927).
[6] MORRIS D. F. C. *Acta Cryst.* **9**, 197 (1956).

* Madelung constants $A\delta_0$ and Aa_0 serve a similar purpose and are for use with δ_0 and a_0 values respectively. δ_0 is the cube root of the molecular volume and a_0 the edge of the cubic unit of structure (for cubic crystal). The parameter values used for different structures are those found experimentally.

TABLE 2.—CRYSTAL ENERGIES OF HALIDES OF DIVALENT ELEMENTS WHICH FORM LARGE SIZED CATIONS (RADIUS 0·95–1·35 Å). CRYSTALLOGRAPHIC AND THERMODYNAMIC DATA RELEVANT FOR THEIR CALCULATION AND THE SECOND IONIZATION POTENTIALS OF THE ELECTROPOSITIVE CONSTITUENTS ARE ALSO GIVEN

	Crystal and structure type		I_2 (eV)	a_0 (Å)	n	U_0 (kcal)	$-\Delta Hf$ (kcal)	$2D$ (kcal)	$-2E$ (kcal)	L (kcal)	I (kcal)	U_{exp} at 25°C (kcal)	U_{theo} (kcal)	Δ (kcal)
I_2 increases ↓	BaF_2	fluorite	10·00	6·187	9·5	559·0	286·9	37·6	−165·0	41·96	364·6	566	561	+5
	SrF_2	fluorite	11·026	5·784	8·5	589·8	290·3	37·6	−165·0	39·2	385·5	588	592	−4
	CaF_2	fluorite	11·87	5·451	8	620·4	290·3	37·6	−165·0	46·04	414·7	624	622	+2
	PbF_2	fluorite	15·03	5·942	9·5	582·1	158·5	37·6	−165·0	46·34	517·6	595	584	+11
	CdF_2	fluorite	16·904	5·40	8·5	631·7	164·9	37·6	−165·0	26·97	597·1	662	634	+28
	HgF_2	fluorite	18·751	5·54	9·5	624·3	95	37·6	−165·0	14·54	673·0	655	626	+29
	$SrCl_2$	fluorite	11·026	7·00	9·5	494·1	198·0	58·0	−174·4	39·2	385·5	506	496	+10
				r_0										
I_2 increases ↓	CaI_2	cadmium iodide	11·87	3·12	10·5	453·4	127·8	51·0	−147·2	46·04	414·7	492	455	+37
	PbI_2	cadmium iodide	15·03	3·13	12	458·1	41·85	51·0	−147·2	46·34	517·6	510	460	+50
	CdI_2	cadmium iodide	16·904	2·99	11	475·4	48·0	51·0	−147·2	26·97	597·1	576	477	+99

Ionization potential values from FINKELNBURG and HUMBACH.[11]
Crystallographic data from WYCKOFF.[12]
Born exponent values due to PAULING.[13]
ΔHf and L values from ROSSINI *et al.*[14] or LONG.[15]
D for fluorine from BARROW and CAUNT, [16] for other halogens from ROSSINI *et al.*[14]
Electron affinities E from PRITCHARD.[17]

[11] FINKELNBURG W. and HUMBACH W. *Naturwiss.*, (1955) **42**, 35.
[12] WYCKOFF R. W. G. "Crystal Structures," Interscience Publishers, New York.
[13] PAULING L. *The Nature of the Chemical Bond*, Cornell Univ. Press (1940).
[14] ROSSINI F. D., WAGMAN D. D., EVANS W. H,. LEVINE S., and JAFFE I. *Selected Values of Chemical Thermodynamic Properties*, National Bureau of Standards, Circular No. 500, Washington (1952).
[15] LONG L. H. *Quart. Rev.* (1953) **7**, 134.
[16] BARROW R. F., and CAUNT A. D. *Proc. Roy. Soc.* A, (1953) **219**, 120.
[17] PRITCHARD H. O. *Chem. Rev.* (1953) **52**, 529.

TABLE 3.—CRYSTAL ENERGIES OF HALIDES OF DIVALENT ELEMENTS WHICH FORM MEDIUM SIZED CATIONS (RADIUS 0·6–0·9Å). CRYSTALLOGRAPHIC AND THERMODYNAMIC DATA RELEVANT FOR THEIR CALCULATION AND THE SECOND IONIZATION POTENTIALS OF THE ELECTROPOSITIVE CONSTITUENTS ARE ALSO GIVEN

	Crystal and structure type		I_2 (eV)	r_0 (Å)	n	U_0 (kcal)	$-\Delta Hf$ (kcal)	$2D$ (kcal)	$-2E$ (kcal)	L (kcal)	I (kcal)	U_{exp} at 25°C (kcal)	U_{theo} (kcal)	Δ (kcal)
I_2 increases ↓	MgF_2	rutile	15·03	2·01	7	688·7	263·5	37·6	−165·0	35·9	522·8	695	684	+11
	MnF_2	rutile	15·64	2·12	8	660·0	189	37·6	−165·0	68·34	531·9	662	662	0
	FeF_2	rutile	16·18	2·06	8	679·0	168	37·6	−165·0	99·8	555·1	696	681	+15
	CoF_2	rutile	17·05	2·04	8	685·8	159	37·6	−165·0	102·0	574·4	708	688	+20
	ZnF_2	rutile	17·96	2·04	8	685·8	176	37·6	−165·0	31·19	630·6	710	688	+22
	NiF_2	rutile	18·15	2·02	8	692·4	159·5	37·6	−165·0	101·61	594·4	728	694	+34
	CuF_2	fluorite	20·29	a_0=5·406	8	625·6	126·9	37·6	−165·0	81·52	646·0	727	627	+100
I_2 increases ↓	$MgBr_2$	cadmium iodide	15·03	2·70	8·5	511·1	123·7	53·4	−161·2	35·9	522·8	575	513	+62
	$MnBr_2$	cadmium iodide	15·64	2·69	9·5	520·1	90·7	53·4	−161·2	68·34	531·9	583	522	+61
	$FeBr_2$	cadmium iodide	16·18	2·65	9·5	528·1	60·02	53·4	−161·2	99·8	555·1	607	530	+77
	$CoBr_2$	cadmium iodide	17·05	2·62	9·5	534·0	55·5	53·4	−161·2	102·0	574·4	624	536	+88
I_2 increases ↓	TiI_2	cadmium iodide	13·57	2·92	10·5	484·5	61	51·0	−147·2	112·6	470·3	548	486	+62
	MgI_2	cadmium iodide	15·03	2·95	9·5	474·3	86·0	51·0	−147·2	35·9	522·8	549	476	+73
	MnI_2	cadmium iodide	15·64	2·95	10·5	479·6	59·3	51·0	−147·2	68·34	531·9	563	481	+82
	FeI_2	cadmium iodide	16·18	2·88	10·5	491·2	29·98	51·0	−147·2	99·8	555·1	589	493	+96
	CoI_2	cadmium iodide	17·05	2·83	10·5	499·9	24·4	51·0	−147·2	102·0	574·4	605	502	+103

For sources of numerical data see Table 2.

caesium, which correspond most closely to the "pure ionic" type of crystal, it provides values for crystal energies in quite good agreement with those obtained using recent thermodynamic data with equation (1).

Moreover, values of U_{theo} provided by the Born equation for the halides of the alkali metals and univalent thallium, copper, and silver are not widely different from those obtained by more refined calculations, which make allowance for van der Waals forces[7,8,9] (mean deviation 4 kcal, maximum deviation 11 kcal).

CRYSTAL ENERGIES OF HALIDES OF DIVALENT ELEMENTS

Tables 2 and 3 enable a comparison of crystal energies of halides of divalent elements derived experimentally by means of the Born-Haber cycle with theoretical values for strict heteropolarity derived with equation (2). Data necessary for the calculation of the crystal energy values are included in the tables. As in previous papers[10,1,2] the compounds are divided into two groups, namely—(i) those derived from large-sized divalent cations (radius 0·95–1·35 Å) and (ii) compounds derived from medium-sized divalent cations (radius 0·6–0·9 Å).

Despite the approximate nature of the Born equation and possible errors in the data used in the calculations, the general trends in Δ values are clear. The results agree reasonably with the view that in the case of crystalline halides regarded as formed via divalent cations of similar radius, increased departure from strict heteropolarity occurs the greater the value of I_2 and the greater the polarizability of the anionic constituent. This concept can be correlated with magnetic, interatomic distance, structural and other evidence.[1,2]

Acknowledgement—The author wishes to express his appreciation to Mr. H. M. POWELL, F.R.S., for information concerning crystal parameters.

[7] HUGGINS M. L. *J. Chem. Phys.* **5**, 143 (1937).
[8] MAYER J. E. *ibid.* **1**, 327 (1933).
[9] MAYER J. E. and LEVY R. B. *ibid.* p. 647.
[10] AHRENS L. H. *Geochim. et Cosmochim. Acta* **3**, 1 (1953).

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FURTHER REMARKS ON THE HYDRATES OF THORIUM TETRAFLUORIDE

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(*Received* 12 *September* 1956)

Abstract—The preparation of $ThF_4 \cdot xH_2O$ (x = 2·5–3·0) and $ThF_4 \cdot yH_2O$ (y = 0·5–2·0) has been reinvestigated and further work on the degradation of these hydrates has been carried out. Three further hydrates have been prepared by the reaction of steam or water with anhydrous thorium tetrafluoride. X-ray crystallographic data are given for these hydrates.

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INTRODUCTION

THE results of previous work on the preparation of the hydrates of thorium tetrafluoride together with the results of our present investigation are best summarized in the form of a table (see Table 1). This table shows both the method of preparation and the inter-relations of the hydrates of thorium tetrafluoride.

The hydrates $ThF_4 \cdot xH_2O$, $ThF_4 \cdot yH_2O$ and $ThF_4 \cdot zH_2O$ were first characterized by D'EYE and BOOTH[1] who also found that small particle size thorium tetrafluoride (phase 1) reacted with water at 100° forming a further hydrate $ThF_4 \cdot 0{\cdot}35H_2O$ (phase 3). According to DAWSON, D'EYE and CHILTON[2] thorium tetrafluoride (phase 1), irrespective of its particle size, was only partially hydrolysed by water at 200–300°; the X-ray photographs showed that the major phase present was phase 3 and that the minor phases were the hydrolysis products thorium oxyfluoride and thoria.

LISTER and BARTLETT[3] stated that large particle size thorium tetrafluoride was not hydrolysed by water at 100°. We confirmed this result and further found that large particle size tetrafluoride did not even react with water at this temperature to form a hydrate. LISTER and BARTLETT also studied the stability of thorium tetrafluoride in steam, and found that samples having a surface area of less than $1 m^2/g$ showed no appreciable hydrolysis up to 250°. However, samples of smaller particle size, such as those prepared by the thermal degradation of the hydrate, started to hydrolyse at 180°. We find that although small particle size thorium tetrafluoride is not hydrolysed by steam at 110° it does react with steam to form a hydrate, phase 3, at this temperature. However, large particle size tetrafluoride neither reacts with steam nor is it hydrolysed by steam up to 270°.

EXPERIMENTAL

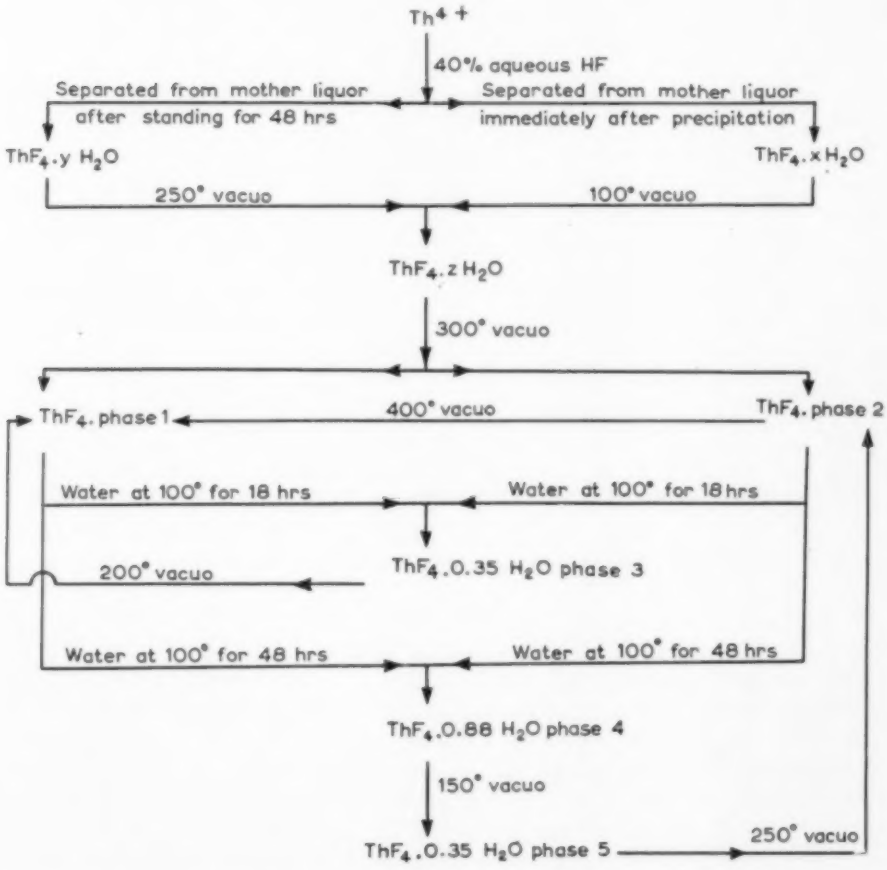
Preparation of the starting materials

(a) *Thorium tetrafluoride hydrates.* D'EYE and BOOTH[1] describe three hydrates of thorium tetrafluoride; pseudo tetragonal $ThF_4 \cdot 2{\cdot}5–3{\cdot}0H_2O$ ($ThF_4 \cdot xH_2O$), orthorhombic $ThF_4 \cdot 0{\cdot}5–2{\cdot}0H_2O$ ($ThF_4 \cdot yH_2O$) and a hydrate of probable composition $ThF_4 \cdot 0{\cdot}25H_2O$ ($ThF_4 \cdot zH_2O$). The first two hydrates were prepared by adding a slight excess of 40% w/w aqueous hydrofluoric acid to a Th^{4+} solution and $ThF_4 \cdot zH_2O$ was prepared by the thermal degradation of the higher hydrates. It was

[1] R. W. M. D'EYE and G. W. BOOTH *J. Inorg. Nucl. Chem.* 1, 326 (1955).
[2] J. K. DAWSON, R. W. M. D'EYE, and D. R. CHILTON U.K.A.E.A. report H.A.R.D. P/16 (1955).
[3] B. A. LISTER and P. M. BARTLETT U.K.A.E.A. report A.E.R.E. C/M 237 (1955).

originally thought that $ThF_4 \cdot zH_2O$ was formed when the hydrate precipitate was dried by washing with acetone and that more rigorous drying conditions produced $ThF_4 \cdot yH_2O$. Further experiments show this is not the case. $ThF_4 \cdot xH_2O$ is obtained when the hydrate precipitate is separated from the mother liquor immediately after precipitation whereas $ThF_4 \cdot yH_2O$ is formed when the hydrate precipitate is allowed to remain in contact with the mother liquor for some time (for example 48 hr).

TABLE 1



X-ray diffraction photographs show that precipitates which have been in contact with the mother liquor for about 16 hr are mixtures of both hydrates.

(b) *Anhydrous thorium tetrafluoride.* Mr. N. KEEN of the Chemistry Division, Harwell kindly supplied samples of thorium tetrafluoride which were prepared by the hydrofluorination of thoria at 450°. Thorium tetrafluoride of smaller particle size ($<0{\cdot}1\ \mu$) was prepared by the thermal degradation of the hydrate. This method is discussed below.

The dehydration of $ThF_4 \cdot x\ H_2O$ and $ThF_4 \cdot yH_2O$ to $ThF_4 \cdot zH_2O$ which could then be dehydrated to thorium tetrafluoride was described in an earlier communication.[1] A more recent study[4] of the dehydration of $ThF_4 \cdot yH_2O$ through $ThF_4 \cdot zH_2O$ to the anhydrous material showed that the removal of water at 300° in air or vacuum gave a small particle size product (phase 2) with a composition $ThF_4 \cdot 0{\cdot}1\text{–}0{\cdot}2H_2O$ and an X-ray diffraction photograph (Fig. 7) different from that of the monoclinic

[4] R. W. M. D'EYE, G. W. BOOTH, and E. A. HARPER U.K.A.E.A. report A.E.R.E. C/R 1735 (1955).

thorium tetrafluoride (phase 1, Figs. 5 and 6) described by ZACHARIASEN.[5] Monoclinic thorium tetrafluoride was formed by heating phase 2 *in vacuo* at 400°. It was suggested that phase 2 was either a metastable form of thorium tetrafluoride or a hydrate of very low water content. We now find that the end product of the dehydration of $ThF_4 \cdot y\,H_2O$ at 300° is either phase 1 or phase 2 and not, as originally thought, always phase 2 (see Table 1).

We have found that materials of small particle size adsorb at least 1% by weight of water when exposed to the atmosphere. Thus our small particle size preparations of thorium tetrafluoride should have analyses in the range $ThF_4 \cdot 0{\cdot}1\text{–}0{\cdot}2H_2O$. This is found to be the case. It is therefore difficult solely by chemical analysis to distinguish between anhydrous tetrafluoride plus adsorbed water and a hydrate of low water content plus, perhaps, also some adsorbed water. However, after annealing phase 1 *in vacuo* at 900° in a platinum apparatus the water content becomes negligibly small although the X-ray diffraction photograph remains the same, except for the expected sharpening of the lines due to the increase in crystallite size (see Figs. 5 and 6). This is reasonable evidence that phase 1 is anhydrous thorium tetrafluoride and is not a hydrate of low water content. The technique of heating samples *in vacuo* in a platinum apparatus will be described in a later communication on the ThO_2/ThF_4 system.

It is not possible to anneal phase 2 as even at 350° *in vacuo* some conversion to phase 1 takes place. It can therefore not be unequivocally shown that phase 2 is another modification of anhydrous thorium tetrafluoride plus adsorbed water.

We conclude that X-ray diffraction photographs are necessary to determine the form of the 300° dehydration product. However, at 400° we have always found that the product is phase 1, i.e. the normal monoclinic variety described by ZACHARIASEN.

(c) *Reaction of thorium tetrafluoride with water.* Thorium tetrafluoride was heated in boiling water at 100° (100 g/litre) for periods up to 72 hours. A slow stream of nitrogen was passed through the sample both to prevent bumping and to agitate the sample. At the end of each experiment the sample was centrifuged and dried either by washing with acetone or by standing in a vacuum desiccator. After drying, the samples were analysed both by chemical and X-ray methods. We found that the method of drying did not affect the water content of the reaction product. Also, the end product was the same irrespective of whether it was separated from the mother liquor at 100° or at room temperature. The mother liquor was titrated with standard alkali to check that hydrolysis of the fluoride had not occurred with the resultant formation of hydrofluoric acid.

ANALYSIS

(a) *Chemical.* The fluorine in the sample was estimated by the pyrohydrolytic method.[6] A current of steam was passed over the sample, contained in a platinum boat, which was heated to 900–1000°C. The resulting hydrofluoric acid-water mixture was condensed and titrated with standard alkali. The steam jet was then removed and the residual oxide ignited in air and weighed as ThO_2. The water content was obtained by difference after determining the thorium and fluorine as above.

(b) *X-ray.* For the X-ray examination of the compounds we used a Guinier-type focusing camera[7] with monochromatized and focused Cu$K\alpha$ radiation from a bent quartz plate. To avoid shrinkage errors in the measurement of the Bragg angle θ, a 0·1 mm scale was contact printed on to the film, before processing.

(c) *Thermogravimetric.* Our earlier work[1] on the hydrates of thorium tetrafluoride showed that a quartz helix type balance could be helpful in determining the composition of the phases formed in a dehydration study, provided that the sample temperature was not increased until the weight loss from the sample had become negligible and that the ambient pressure in the apparatus was 10^{-4} mm. As the sample was in powder form the rate of evaporation of the vapour phase was controlled

[5] W. H. ZACHARIASEN *Acta Cryst.* **2**, 388 (1949).
[6] G. M. GILLIES, N. J. KEEN, B. A. J LISTER, and D. REES U.K.A.E.A. report A.E.R.E. C/M 225 (1954).
[7] R. W. M. D'EYE U.K.A.E.A. report A.E.R.E. C/R 1524 (1954); *Nature* **175**, 623 (1955).

by the rate of diffusion of the vapour through a layer of dissociated material as well as by the dissociation pressure. The results are therefore not as unambiguous as when the rate of evaporation is controlled solely by the dissociation pressure.

It seems that composition-temperature diagrams obtained when the sample is heated in air at a rate of 3–5° per minute may give misleading results. However, MURPHY, BHARADWAJ, and MALLYA[8] heated their sample of sodium phosphate dodecahydrate in air at this rate and still obtained results compatible with previous work.

The apparatus used in the present work was similar to that used previously.[1,9] Degradation runs were carried out both in air and *in vacuo*. The quartz spiral spring had an extension of about 1 mm per mg and the weight of sample used was approximately 100 mg. A liquid nitrogen trap was close to the sample to collect the water vapour, thus preventing errors due to water adsorption on the spring and re-adsorption by the specimen. The time taken for a degradation experiment was between one and two weeks.

RESULTS AND DISCUSSION

(a) *Formation of anhydrous thorium tetrafluoride*. Thorium tetrafluoride hydrates degrade at 300° under apparently identical conditions to form either phase 1 or phase 2 (Table 1). It is perhaps possible to explain this result on the basis of GARNER'S[10] model of the removal of water from a hydrate. During the dehydration of a hydrate crystal *in vacuo* the water molecules evaporate from the surface leaving a dehydrated ionic network. This structure is usually unstable and undergoes rearrangement to form a phase with no definite crystal structure called the transition or amorphous layer. A further rearrangement then occurs giving crystalline nuclei of a new phase. When there is the opportunity for the formation of several products as nuclei in the amorphous layer, as in our particular case, the choice as to which will form appears to depend on the degree to which water vapour is held up by impedance in this amorphous layer.

(b) *The reaction of thorium tetrafluoride* (*phase* 1) *with water and steam*. Some results of heating phase 1 with water and steam are given in Tables 1 and 2. Phase 1, with a particle size greater than 1 μ, does not react with water at 100° nor with steam up to 270° to form hydrates. Evidence that the sample had also not hydrolysed was provided by the Th/F ratio remaining at $\frac{1}{4}$, the mother liquor containing no hydrofluoric acid and the X-ray diffraction photographs showing no thoria or thorium oxyfluoride.

Similar results show that small particle size tetrafluoride, prepared by thermal degradation of the hydrate, does not hydrolyse in water or steam at 110°. However, the X-ray diffraction photograph (Fig. 8) of the end product of heating small particle size tetrafluoride with water at 100° for 18 hours is similar to but not the same as the diffraction pattern of the starting material (Fig. 5). The diffraction pattern is not similar to the diffraction pattern of $ThF_4 \cdot xH_2O$ (Fig. 11) nor $ThF_4 \cdot yH_2O$ (Fig. 12). The chemical analysis gave compositions in the range $ThF_4 \cdot 0{\cdot}33$–$0{\cdot}5H_2O$. The exact composition is difficult to determine owing to the water adsorption on the surface

[8] A. R. VASUDEVA MURPHY, D. S. BHARADWAJ, and R. M. MALLYA *Chem. and Ind.* 300 (1956).
[9] R. W. M. D'EYE and P. G. SELLMAN U.K.A.E.A. report A.E.R.E. C/R 1077 (1953); *J. Chem. Soc.* 3760 (1954).
[10] W. E. GARNER *Chemistry of the Solid State*, Chap. 8, Butterworth's Scientific Publications (1955).

FIG. 5.—Phase 1.

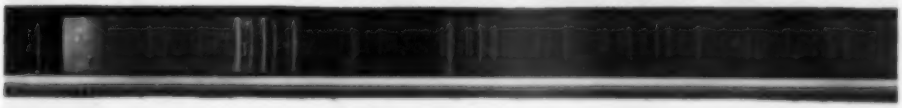


FIG. 6.—Phase 1.

FIG. 7.—Phase 2.

FIG. 8.—Phase 3.

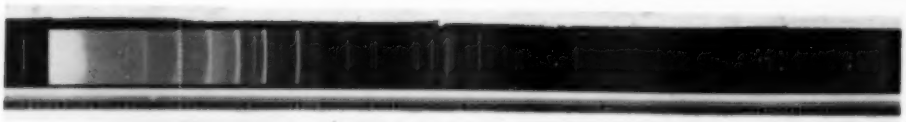


FIG. 9.—Phase 4.

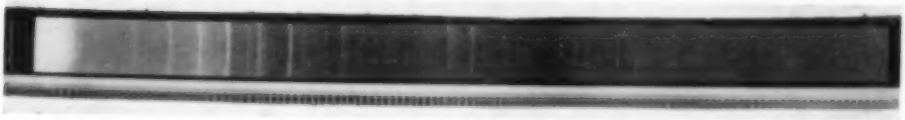


FIG. 10.—Phase 5.

FIG. 11.—$ThF_4 \cdot xH_2O$

FIG. 12.—$ThF_4 \cdot yH_2O$

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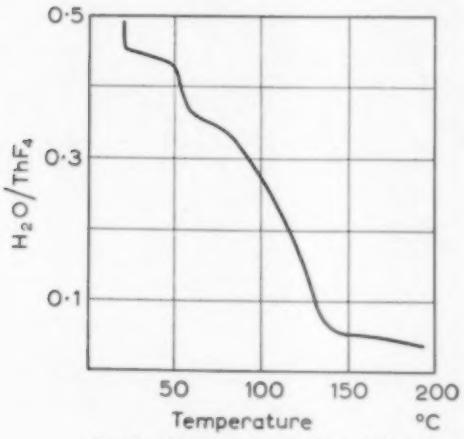

FIG. 1.—Vacuum degradation of phase 3.

TABLE 2

Initial material	Treatment	Analysis	
		Chemical H_2O/ThF_4 ratio	X-ray
Phase 1 ThF_4[a] (particle $>1\ \mu$)	Water at 100° for 18 hr	0·05	Phase 1
Phase 1 ThF_4[a] (particle $>1\ \mu$)	Steam at 270° for 2½ hr	0	Phase 1
Phase 1 ThF_4[b] (particle $<1\ \mu$)	Water at 100° for 6 hr	0·48	Phase 3
Phase 1 ThF_4[b] (particle $<1\ \mu$)	Water at 100° for 18 hr	0·37	Phase 3
Phase 1 Th_4[b] (particle $<1\ \mu$)	Water at 100° for 48 hr	0·90	Phase 4
Phase 1 ThF_4[b] (particle $<1\ \mu$)	Steam at 110° for 1 hr	0·10	Phase 1
Phase 1 ThF_4[b] (particle $<1\ \mu$)	Steam at 110° for 4 hr	0·37	Phase 3
Phase 2 ThF_4[c]	Water at 100° for 18 hr	0·4	Phase 3
Phase 2 ThF_4[c]	Water at 100° for 24 hr	0·9	Phase 4
Phase 2 ThF_4[c]	Water at 100° for 48 hr	0·9	Phase 4
Phase 2 ThF_4[c]	Water at 100° for 72 hr	1·03	Phase 4
Phase 2 ThF_4[c]	Steam at 110° for 4 hr	0·48	Phase 3
Phase 3	75° in air[d] to const. wt.	0·33	Phase 3
Phase 3	150° in air to const. wt.[d]	0·10	Phase 1
Phase 3	100° *in vacuo* for 16 hr	0·37	Phase 3
Phase 3	120° *in vacuo* for 16 hr	0·24	Poor photograph
Phase 3	200° *in vacuo* for 16 hr	—	Phase 1
Phase 4	150° in air to const. wt.	0·80	Phase 4
Phase 4	175° in air to const. wt.	0·48	Phase 5
Phase 5	200° in air to const. wt.	0·12	Phase 2
Phase 4	100° *in vacuo* for 24 hr	0·84	Phase 4
Phase 4	150° *in vacuo* for 24 hr	0·40	Phase 5
Phase 5	200° *in vacuo* for 24 hr	0·20	Poor photograph
Phase 5	250° *in vacuo* for 24 hr	—	Phase 2
Phase 2	400° *in vacuo* for 24 hr	—	Phase 1

[a] ThF_4 prepared by hydrofluorination of ThO_2 at 450°.
[b] and [c] ThF_4 prepared by the thermal degradation of hydrate at 300°.
[d] Heating runs carried out in platinum containers.

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of the particles. However, the thermogravimetric results indicate a composition close to $ThF_4 \cdot 0{\cdot}35H_2O$ (Fig. 1). This compound is referred to as phase 3 in Tables 1 and 2.

As thorium tetrafluoride (phase 1) is isostructural[5] with uranium tetrafluoride, the case of water entering the thorium tetrafluoride lattice might be analogous to that of fluorine entering the uranium tetrafluoride lattice. Agron, Grenall and Kunin[11] identified a compound with the composition U_4F_{17}. The complex X-ray diffraction pattern of this compound was not indexed but because of its similarity to the diffraction pattern of uranium tetrafluoride it was referred to as a "distorted" UF_4-type structure. Uranium tetrafluoride is monoclinic with twelve molecules per unit cell. In each unit cell there are twelve "holes" which are not quite large enough to accommodate fluorine atoms. Burbank[12] has suggested that a distortion of the structure should allow fluorine atoms to enter the lattice. Thus by filling three of the "holes" with fluorine atoms the composition changes to U_4F_{17} and the distortion necessary to permit this causes the slight change in the diffraction pattern.

In our case the diffraction pattern of thorium tetrafluoride hydrate (phase 3) is similar to that of anhydrous thorium tetrafluoride (phase 1). Thus if four "holes" in the thorium tetrafluoride lattice were filled by water molecules the composition would become $ThF_4 \cdot 0{\cdot}33H_2O$ and the resultant lattice distortion necessary to permit this would account for the slight change in the diffraction pattern.

Table 3

Intensity	*hkl*	$\sin^2\theta_o$	$ThF_4 \cdot 0{\cdot}88H_2O$ Phase 4		*hkl*	$\sin^2\theta_o$	$\sin^2\theta_c$
			$\sin^2\theta_c$	Intensity			
vvw	100	0·0089	0·0093	w	212	0·0844	0·0838
vvw	001	0·0108	0·0108	vw	310	0·0865	0·0869
w+	110	0·0122	0·0124	w	320	0·0968	0·0963
	020		0·0126	w	151	0·0991	0·0991
m	101	0·0199	0·0201	vvw	142	0·1037	0·1033
m	030	0·0285	0·0284	vvw	232	0·1088	0·1090
vvw	121	0·0322	0·0327	vvw	113	0·1101	0·1103
m	200	0·0371	0·0372		023		0·1105
m	130	0·0378	0·0377	vvw	060	0·1137	0·1138
m−	002	0·0434	0·0434	w	123	0·1203	0·1198
vvw	012	0·0462	0·0466	w	160	0·1229	0·1231
m	201	0·0476	0·0480		331		0·1229
vvw	131	0·0490	0·0485		052		0·1224
vvw	040	0·0505	0·0506	vvw	251	0·1270	0·1270
vvw	102	0·0524	0·0527		302		0·1271
m	221	0·0608	0·0606	w	312	0·1302	0·1303
m−	041	0·0614	0·0614	m	152	0·1318	0·1317
vvw	300	0·0833	0·0837		242		0·1312
				w	203	0·1350	0·1351

[11] P. Agron, A. Grenall, R. Kunin, and S. Weller U.S.A.E.C. report MDDC—1588 (1948).
[12] R. D. Burbank A.E.C.D. 3216 (1951).

X-ray diffraction photographs (Fig. 9) of the end product of the reaction between small particle size tetrafluoride and water at 100° for 48 hours show a further phase called phase 4. This has a composition varying between $ThF_4 \cdot 0{\cdot}9$–$1{\cdot}0H_2O$. The thermogravimetric results indicate a composition close to $ThF_4 \cdot 0{\cdot}88H_2O$ (Figs. 3 and 4).

The X-ray diffraction photograph of phase 4 is complex with a large number of

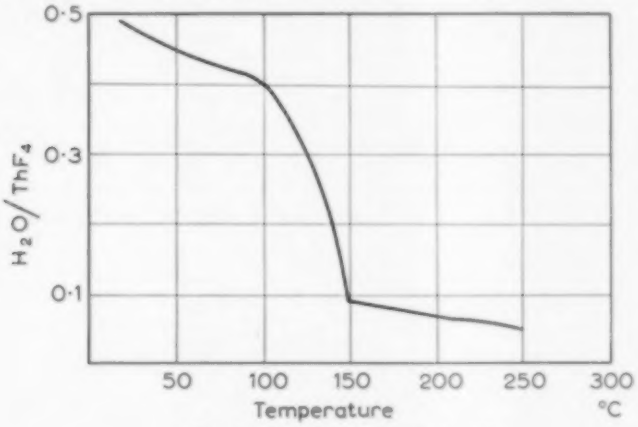

FIG. 2.—Air degradation of phase 3.

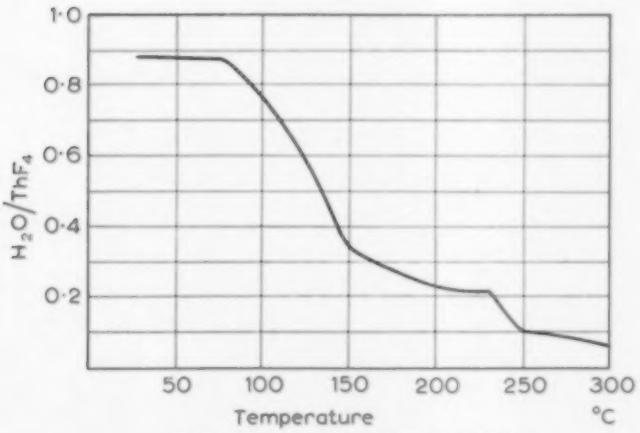

FIG. 3.—Vacuum degradation of phase 4.

faint lines. The observed $\sin^2\theta$ values were found to fit the quadratic form $\sin^2\theta_{hkl} = 0{\cdot}0093h^2 + 0{\cdot}00316k^2 + 0{\cdot}01085l^2$ which corresponds to an orthorhombic cell with $a = 7{\cdot}98 \pm 0{\cdot}01$ kX, $b = 13{\cdot}69 \pm 0{\cdot}05$ kX, $c = 7{\cdot}39 \pm 0{\cdot}01$ kX. The unit cell volume is 806 kX^3. The cell can therefore contain eight molecular units of $ThF_4 \cdot 1{\cdot}0H_2O$ or $ThF_4 \cdot 0{\cdot}88H_2O$. The latter value agrees with the value obtained by the thermogravimetric studies. The calculated values of $\sin^2\theta_c$ are seen from Table 3 to be in fair agreement with the observed $\sin^2\theta_o$ values. Although there are apparently no

systematic absences in the observed indices of the reflections, only about 56% of the total possible number of reflections are observed up to $\theta = 21°$. This might be caused either by a number of reflections having low structure factors and therefore being too faint to be observed on the diffraction photograph or by the proposed cell being a pseudo-cell. However, further work must be carried out to check that our orthorhombic indexing of the pattern is correct.

(c) *The reaction of thorium tetrafluoride (phase 2) with water and steam.* Some results of heating phase 2 with water and steam are shown in tables 1 and 2. Phase 2 does not hydrolyse in water and steam at the temperatures used in our experiments. However, phase 3, described in the previous section, was formed when phase 2 was heated either with water for 18 hours or with steam for 4 hours. Heating for longer periods of time produced phase 4, also described in the previous section.

(d) *Thermal degradation of phase 3 in air and vacuum.* Phase 3 degrades when heated in vacuum or air to phase 1 (see Tables 1 and 2). The thermogravimetric curves for these degradations are shown in Figs. 2 and 3 respectively. The X-ray diffraction study shows that the break in the graph (Fig. 1) at about the composition $ThF_4 \cdot 0{\cdot}35H_2O$ does not represent a phase change. The water present above this composition is probably adsorbed surface water. Similarly the break in the graph (Fig. 2) at about a composition $ThF_4 \cdot 0{\cdot}4H_2O$ does not represent a phase change. The compositions at which breaks in the graphs occur are seen to be slightly different according as to whether the substance was degraded in vacuum or air. We estimate that the error in the determination of the water content of a hydrate using a thermogravimetric method is $\pm 0{\cdot}02$ water molecules. Also in the experimental section of this paper we suggested that results obtained by thermogravimetric methods, when the sample is in powder form, are not completely unambiguous. Thus the exact composition of phase 3 remains in some doubt although we think it is close to $ThF_4 \cdot 0{\cdot}33H_2O$.

The break in the graphs at about the composition $ThF_4 \cdot 0{\cdot}05$–$0{\cdot}08H_2O$ represents the formation of phase 1. The water present at this composition is probably adsorbed surface water. The thermogravimetric results show that this water is not removed below 300°.

(e) *Thermal degradation of phase 4 in air and vacuum.* It is seen from Tables 1 and 2 that phase 4 degrades, when heated to constant weight in air at 175° and in vacuum to 150°, to a composition $ThF_4 \cdot 0{\cdot}4$–$0{\cdot}5H_2O$. The X-ray diffraction pattern of this material (Fig. 10) is similar to but not the same as the diffraction pattern of phase 4. We refer to this further hydrate as phase 5. The $\sin^2\theta$ values and observed intensities for the stronger lines are shown in Table 4 for identification purposes. We have not yet unambiguously indexed this diffraction pattern. The symmetry might be pseudo-hexagonal with $a_H = 13{\cdot}86 \pm 0{\cdot}05$k X, $c_H = 8{\cdot}55 \pm 0{\cdot}02$ kX. The a_H parameter of this pseudo-cell is roughly equal to $\sqrt{3}\, a_0$ and to b_0 of the orthorhombic cell of phase 4. Further crystallographic studies are needed in order to be certain of the correct structures for both phase 4 and 5. It might then be possible to see that the structures of these two hydrates are closely related and that both are based on a small hexagonal cell.

At 200° phase 5 degrades to phase 2. Thermogravimetric curves for the degradation of phase 4 are shown in Figs. 3 and 4 respectively. In both Figs. the first break in the curves occurs at a composition approximately $ThF_4 \cdot 0{\cdot}88H_2O$

TABLE 4

I_o	$\sin^2\theta$	$ThF_4 \cdot 0{\cdot}35H_2O$ Phase 5		I_o	$\sin^2\theta$
		I_o	$\sin^2\theta$		
vw	0·0124	m	0·0376	w	0·0490
w+	0·0202	vw	0·0446	m	0·0617
w+	0·0287	w	0·0482	w−	0·0858
				vw	0·0954

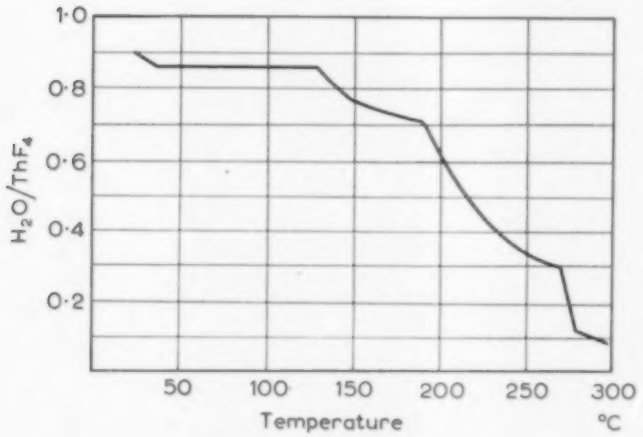

FIG. 4.—Air degradation of phase 4.

which represents the probable true composition of phase 4. The break in the curves at about a composition $ThF_4 \cdot 0{\cdot}33H_2O$ represents the formation of phase 5.

As previously stated the thermogravimetric results give a lower value for the water content of these hydrate phases than that obtained by chemical analysis. This is because in the latter method the samples are handled in air at room temperature and therefore adsorb water.

Acknowledgement—The authors wish to thank Dr. B. A. J. LISTER for permission to discuss his results on the action of water and steam on thorium tetrafluoride prior to publication.

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THE PREPARATION OF GERMANE*

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(*Received* 20 *September* 1956)

Abstract—Germane is conveniently prepared by reduction of an aqueous acidic solution of germanium oxide with sodium borohydride.

INTRODUCTION

PREVIOUS preparations of germane have used the reaction of magnesium germanide with hydrochloric acid[1] or with ammonium bromide in liquid ammonia.[2] Also, germanium tetrachloride may be reduced with lithium aluminium hydride in ether,[3] but the yield is less than 30%. The preparation of stannane by dropping an aqueous solution of sodium borohydride into a solution of tin(II) chloride in dilute hydrochloric acid[4] led us to attempt to prepare germane by a similar reaction. We have found that germane is quite conveniently prepared in 60–75% yields using this method. The unpurified germane was found to contain about 0·6% by volume of digermane.

In an attempt to prepare monodeuterogermane this reaction was carried out in a solution containing 45% deuterium oxide. By estimation from the intensities of infra-red bands of the products it was found that 20 to 25% of the germane molecules contained a deuterium atom. This is interesting in that it indicates that there exists some mechanism of formation of germane other than hydride transfer to the germanium from the borohydride ion if exchange of hydrogen of borohydride ion with water is excluded (sodium borohydride has been shown not to exchange with deuterium oxide at pH = 12).[5] A better method of preparing pure monodeuterogermane was found in the reduction of sodium germanyl[2] with deuterium chloride in di-*n*-butyl ether. The product of this reaction gave an infra-red spectrum in the sodium chloride region which was identical with that reported for monodeuterogermane prepared from trichlorogermane by reaction with lithium aluminium deuteride.[6]

Attempts to prepare plumbane by action of sodium borohydride on divalent lead under similar conditions have failed to produce appreciable gaseous products nor was absorption in the infra-red observed where the lead-hydrogen stretching frequency would be expected. A hydrogen sulphide test on material in the trap where plumbane would have collected gave a slight but dubious test for lead.

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[1] L. M. DENNIS, R. B. COREY, and R. W. MOORE *J. Amer. Chem. Soc.* **46**, 657 (1924).
[2] C. A. KRAUS and E. S. CARNEY *J. Amer. Chem. Soc.* **56**, 765 (1934).
[3] A. E. FINHOLT, A. C. BOND JR., K. E. WILZBACH, and H. I. SCHLESINGER *J. Amer. Chem. Soc.* **69** 2692 (1947).
[4] G. W. SCHAEFFER and M. EMELIUS *J. Amer. Chem. Soc.* **76**, 1204 (1954).
[5] R. P. GIRORDOT and R. W. PARRY *J. Amer. Chem. Soc.* **73**, 2368 (1951).
[6] L. P. LINDEMAN and M. K. WILSON *Z. physik. Chem.* (in press).

EXPERIMENTAL

The reaction was carried out in a three-hundred millilitre, three-necked flask, equipped with dropping funnel, magnetic stirrer, and a reflux condenser. The condenser led to a manifold with a mercury manometer and thence through two U-traps to a vacuum pump. The first trap was made from 20-mm glass tubing while the second which connected directly to the pump was made from 7-mm tubing.

Germanium oxide (0·2995 g) was dissolved in boiling 1 M hydrobromic acid (150 ml) in the flask. The solution was then cooled with an ice bath. Sodium borohydride (2 g) dissolved in water (40 ml) was placed in the dropping funnel. Both traps were placed in liquid nitrogen. The second trap was evacuated and the stopcock between it and the first trap was set to give a slow leak. When the pressure in the flask, manifold, and first trap was reduced to 10 or 20 cm the sodium borohydride solution was slowly dropped into the flask to maintain this pressure. In all, 6 g of sodium borohydride was added in 2 g portions. After the addition of each portion, the material in the first trap volatile at −78°C was transferred to the second. Of this crude product 58% was collected with the first portion of sodium borohydride and 92% with the first two portions. The crude germane was then purified by distillation through a trap at −100°C to give 550 ml of gas at 71 mm and 27°C or 47·2 ml S.T.P., a yield of 73%. There was no appreciable germanium left in solution: a slight metallic mirror on the inside of the reaction flask indicated the remaining germanium had been reduced to the element.

The germane was found to be quite pure by examination of its infra-red spectrum. In another experiment 700 ml (S.T.P.) of germane were prepared and it was carefully fractionated through a trap held at −140°C. The material in the trap amounted to 0·43 ml (S.T.P.) or 0·6% by volume of the original gas. It was found to be digermane by comparison of its infra-red spectrum with that reported previously.[7]

[7] D. A. Dows and R. M. Hexter *J. Chem. Phys.* **24**, 1029 (1956).

J.inorg. Nucl. Chem., 1957, Vol. 4, pp. 24 to 29. Pergamon Press Ltd., London

SIMPLE AND COMPLEX OXYHALIDES OF RUTHENIUM AND OSMIUM

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Abstract—Attempts to prepare simple and complex oxyfluorides of ruthenium have failed. Osmium is shown to form an octavalent oxyfluoride, OsO_3F_2, the parent of the trifluoroperperosmates, $M^IOsO_3F_2$ (M^I = K, Cs, Ag). The preparation of an oxychloride of hexavalent osmium, $OsOCl_4$, is also described together with its reaction with hydrochloric acid under varying conditions. Structural and magnetic data are presented for compounds of the type $Cs_2MO_2Cl_4$ (M = Ru, Os).

ALTHOUGH all the six platinum metals form well-characterized binary and complex compounds with the halogens, ruthenium and osmium alone show a readiness to combine with oxygen to form stable oxides. This feature suggests that these two elements should be able to form compounds containing both oxygen and a halogen and this premise is borne out by a survey of the rather scanty literature on the subject.

Complex oxyhalides of both ruthenium and osmium are known. These include the hexavalent tetrachlororuthenates $M_2^IRuO_2Cl_4$ (M^I = Rb, Cs,[1] and H[2]) and the corresponding tetrachloro- and tetrabromo-osmates $M_2^IOsO_2X_4$ (M^I = K, NH_4; X = Cl, Br[3]); more recent work has disclosed that the compound "K_2RuCl_5OH" is to be regarded as a complex oxyhalide of tetravalent ruthenium with the constitution $K_4Ru_2OCl_{10}.H_2O$.[4] No true simple oxyhalides have been reported, however, beyond some separated from aqueous solutions which contain hydrogen in addition, either as hydroxyl or water of constitution. Reactions which might conceivably have led to the formation of an oxyhalide failed; for example, the chlorination of ruthenium dioxide[5] gave only the binary chloride. In this connection it may be noted that the claim of RUFF[6] to have produced an oxyfluoride of iridium, $IrOF_4$, has recently been shown to be ill-founded.[7]

EXPERIMENTAL

Two general experimental approaches have been employed: (1) the fluorination, using both elementary fluorine and liquid fluorides, of oxygenated derivatives of the elements, and (2) the action of gaseous halogen/oxygen mixtures on the metal.

Oxyhalides of ruthenium

(1) *Reaction of ruthenium dioxide with elementary fluorine.* Anhydrous ruthenium dioxide was prepared by igniting metallic sponge in a current of oxygen at 1000°. The product, in a nickel boat, was transferred to a silica reaction tube and heated to 150° in a stream of fluorine (4 litres/hr), freed from hydrogen fluoride, and suitably diluted with nitrogen. Bright green droplets of ruthenium pentafluoride distilled from the reaction zone as the sole product of the reaction.

(2) *The action of bromine pentafluoride on ruthenium tetroxide.* Bromine pentafluoride was

[1] J. L. HOWE *J. Amer. Chem. Soc.* **23**, 779 (1901).
[2] S. AOYAMA *Z. anorg. Chem.* **138**, 252 (1924).
[3] L. WINTREBERT *Ann. Chim. Phys.* [vii] **28**, 54, 86 (1903).
[4] A. McL. MATHIESON, D. P. MELLOR, and N. C. STEPHENSON *Acta Cryst.* **5**, 185 (1952).
[5] H. REMY and T. WAGNER *Z. anorg. Chem.* **157**, 344 (1926).
[6] O. RUFF and J. FISCHER *Z. anorg. Chem.* **179**, 161 (1929).
[7] P. L. ROBINSON and G. J. WESTLAND *J. Chem. Soc.* (in press).

prepared by passing a mixture of bromine vapour and fluorine through a nickel tube heated to 200°, and the crude product purified by trap-to-trap distillation from solid potassium fluoride (to retain any bromine trifluoride) in a stream of dilute fluorine. Ruthenium tetroxide (0·5 g), prepared according to MARTIN,[8] was dried over phosphoric oxide and transferred in a vacuum to a Pyrex-glass reaction bulb containing 20 ml of bromine pentafluoride. At temperatures below 0° the tetroxide dissolved to a clear yellow solution in the pentafluoride, but, as the temperature rose, a deep green colour developed which changed, through blue, finally to brown and meanwhile oxygen was copiously evolved. Removal of the excess reagent in a vacuum at room temperature left a pale pink solid which, on heating to 114° in a vacuum, melted and evolved bromine pentafluoride together with a vapour which formed green droplets of ruthenium pentafluoride. Evidently, the solid consisted of an addition compound between ruthenium pentafluoride and bromine pentafluoride, possibly of the type $RuF_5 \cdot BrF_5$ and similar to the one formed with bromine trifluoride.[9]

(3) *Potassium perruthenate and bromine trifluoride.* Excess bromine trifluoride, prepared as described previously,[9] was condensed in a vacuum on to 0·2 g of potassium perruthenate. A smooth evolution of oxygen took place on warming to room temperature and a white precipitate appeared in the pale yellow liquid. Excess reagent was removed in a vacuum and the product dried at 100°. A partial analysis for fluorine only, and a qualitative examination of its X-ray photograph, established the material to be potassium hexafluororuthenate(V), $KRuF_6$. Found: F = 45·0%; calc. for $KRuF_6$, F = 44·9%.

(4) *Caesium tetrachlororuthenate(VI).* This salt was prepared according to HOWE.[1] Found: Cl = 26·1%; calc. for $Cs_2RuO_2Cl_4$; Cl = 26·2%. An X-ray powder photograph of it taken in a 19-cm camera using Fe$K\alpha$ radiation, established a cubic structure with $a = 10{\cdot}07$ Å. A measurement of the magnetic moment, using the Gouy method, showed it to be diamagnetic. Water produced instant hydrolysis according to the equation

$$2Cs_2RuO_2Cl_4 + 2H_2O = RuO_4 + RuO_2 + 4CsCl + 4HCl$$

but the crystals can be recovered unchanged from dilute hydrochloric-acid solution. Boiling 10 N hydrochloric acid brings about reduction with precipitation of black, crystalline caesium hexachlororuthenate(IV), Cs_2RuCl_6. This also is cubic with $a = 10{\cdot}22$ Å.

Elementary fluorine reacted vigorously at about 150° with $Cs_2RuO_2Cl_4$ to give a pale blue solid which X-ray examination showed to contain caesium hexafluororuthenate(V), $CsRuF_6$, as the main constituent. When treated with liquid, anhydrous hydrofluoric acid, $Cs_2RuO_2Cl_4$ turned black but no hydrogen chloride was evolved.

Oxyhalides of osmium

(1) *Osmium oxytetrachloride.* Osmium metal powder (0·3 g) was spread in a shallow layer along the length of a glass reaction vessel and heated to 400° in a stream of dry chlorine and oxygen in which the gases were present in the volume ratio 8 : 1, respectively. Volatile products were collected in a U-tube cooled to −10°. When all the metal had been consumed, the contents of the U-tube were allowed to come to room temperature and the osmium tetroxide present was removed under a pressure of 10^{-2} mm. The dark brown residue of crude osmium oxytetrachloride was then purified by distillation in a vacuum. The yield, based on osmium taken, was 70%. Found: Cl = 41·0%. $OsOCl_4$ requires Cl = 40·8%.

Osmium oxytetrachloride is a dark brown diamagnetic solid which, on careful heating in a vacuum, sublimes as long, needle-shaped crystals, m.p. 32°. The liquid boils above 200° and produces a deep yellow vapour.

(2) *Caesium tetrachloro-osmate(VI).* Osmium oxytetrachloride was dissolved in excess 10 N hydrochloric acid cooled to −20° and a concentrated solution of caesium chloride was added to the deep green solution. The dark green precipitate was separated on a sintered glass disk and washed with cold 10 N hydrochloric acid. Found: Cl = 26·0, 25·4, 24.8%. $Cs_2OsO_2Cl_4$ requires Cl = 22·5%, Cs_2OsOCl_5 requires Cl = 31·1%. The specimen containing 26·0% chlorine was cubic with $a = 10{\cdot}12$ Å. On warming the crystals with excess 2 N hydrochloric acid, they dissolved to an orange solution which, on cooling, deposited pure caesium tetrachloro-osmate(VI) as a buff powder. Found: Cl = 22·4%. The cubic lattice is iso-dimensional with $Cs_2RuO_2Cl_4$. A measurement of the magnetic moment of this material showed it to be diamagnetic. Boiling with 10 N

[8] F. S. MARTIN *J. Chem. Soc.* 3055 (1952).
[9] M. A. HEPWORTH, R. D. PEACOCK, and P. L. ROBINSON *J. Chem. Soc.* 1197 (1954).

hydrochloric acid brings about reduction to the red caesium hexachloro-osmate(IV), Cs_2OsCl_6. Found: Cl = 31·5%. Cs_2OsCl_6 requires Cl = 31·8%. Cs_2OsCl_6 is cubic and iso-dimensional with Cs_2RuCl_6.

(3) *Potassium, caesium, and silver trifluoroperperosmates.* A known weight of osmium metal was quantitatively converted to the tetroxide by burning in pure dry oxygen and transferring the product in a vacuum to a break-seal vessel. This, in turn, was attached to a train of traps which allowed the tetroxide, together with an excess of bromine trifluoride, to be condensed in a vacuum into a bulb containing an equivalent of potassium or caesium bromide or, in the case of silver, of silver iodate. In all the reactions there was a smooth evolution of oxygen on warming to room temperature. Those involving alkali metals formed salts which gave orange solutions in the excess of bromine trifluoride. The silver salt proved to be less soluble, and separated as deep orange crystals. The excess solvent was removed in a vacuum at room temperature and the orange salts were dried at 40–50° for several hours. Found: F = 20·0%, E = 317. $KOsO_3F_3$ requires F = 17·0%, E = 334. Iodometric titration showed that 3·9 equivalents of iodine were liberated per the eqivalent of osmium, indicating that the valency of osmium in the salt was 4 + 3·9 = 8. Found: F = 15·1%, E = 454. $CsOsO_3F_3$ requires F = 13·3%, E = 428. 4·2 equivalents of iodine were liberated per equivalent of osmium. Found: F = 13·8, Ag = 26·7%. $AgOsO_3F_3$ requires F = 14·1, Ag = 26·8%. An X-ray powder photograph of the silver salt revealed a complex pattern which could not be indexed.

(4) *Osmium trioxydifluoride.* (a) When two equivalents of osmium tetroxide were allowed to react with one of potassium bromide under the conditions just described, an orange residue remained in the reaction bulb after the removal of the excess of bromine trifluoride at room temperature. This, on heating to 100° in a vacuum, produced an orange sublimate which by a suitable application of heat was driven into a collecting arm of the apparatus. Found: F = 13·5, 14·2%. OsO_3F_2 requires F = 13·8%. 4 equivalents of iodine were liberated per equivalent of osmium, hence the valency of the osmium is 4 + 4 = 8.

A little of the preparation was introduced, by tapping, into a melting-point tube attached to the main apparatus, and the melting-point, taken in the usual way, at atmospheric pressure was found to be 170–172°. The material melted to a red liquid; the vapour pressure at the melting-point was appreciable, since, at that temperature, a quantity of it sublimed on to the cooler surfaces of the apparatus. The material appears to be identical with the orange sublimate formed during the heating of the product from the action of bromine trifluoride on osmium tetrabromide,[10] which probably arises from either a trace of moisture or some oxy-compound in the bromide.

(b) Osmium-metal sponge was fluorinated in an alumina apparatus of the kind which has been described previously,[10] using oxygen as carrier gas in the volume ratio oxygen : fluorine of 2 : 1. Under these conditions, OsO_3F_2 was almost the sole product of the reaction. Higher oxygen concentrations lead to the production of some osmium tetroxide, b.p. 130°, and, conversely, higher fluorine concentrations lead to the formation of some octafluoride, b.p. 47°; incidentally, both of these materials, by reason of their greater volatility, may be easily removed from the oxyfluoride by distillation.

DISCUSSION

In contrast to oxygen, with which ruthenium forms a tetroxide, fluorine is unable to excite the octavalent state of the element, the highest known fluorides being the pentafluoride, RuF_5, and its derivatives the hexafluororuthenates(V). However, since the intermediate valencies six and seven are so well characterized in the ruthenates and their derivatives and the perruthennte, respectively, it might be expected that either simple or complex oxyfluorides of Ru(VI), Ru(VII), or perhaps even of Ru(VIII) could be prepared. Many analogies exist which support this view. Thus, chromium forms a pentafluoride, CrF_5, and also forms the hexavalent oxyfluoride CrO_2F_2;[11] manganese forms a trifluoride, MnF_3, and the heptavalent oxyfluoride, MnO_3F, recently observed;[12] and rhenium the hexafluoride ReF_6 and all three possible heptavalent oxyfluorides $ReOF_5$, ReO_2F_3,[13] and ReO_3F.[12]

[10] M. A. HEPWORTH, P. L. ROBINSON, and G. J. WESTLAND *J. Chem. Soc.* 4269 (1954).
[11] A. ENGELBRECHT and A. V. GROSSE *J. Amer. Chem. Soc.* **74**, 5262 (1952).
[12] A. ENGELBRECHT and A. V. GROSSE *J. Amer. Chem. Soc.* **76**, 2042 (1954).

Nevertheless, a comprehensive search involving many reactions which might have been expected to produce oxyfluorides of ruthenium resulted, in every instance, in the formation of the pentafluoride. Attempts to stabilize the expected oxyfluoride as part of a co-ordination compound by fluorinating potassium perruthenate and caesium tetrachlororuthenate led in each case to the complete elimination of oxygen and the formation of the corresponding hexafluororuthenate(V). These two observations accord with those of WEISE and KLEMM,[14] who found that the fluorination of "K_2RuCl_5OH," or more properly $K_4Ru_2OCl_{10}$, H_2O, gave "K_2RuF_8," that is $KRuF_6 + KF_2$. Milder fluorinating conditions, secured by using anhydrous hydrogen fluoride, proved no more effective, and it must be concluded that oxyfluorides of ruthenium, if they exist, are very unstable substances.

The facts about ruthenium just disclosed do little to suggest that osmium, the element immediately below it in the Periodic Table, should yield oxyhalides. But the evidence from the horizontally placed rhenium is more encouraging. Both rhenium and osmium have a great affinity for oxygen, exemplified by the extremely stable perrhenate ion and the tetroxide of osmium, and, in addition, each forms a set of well characterized halides. Furthermore, oxychlorides and oxyfluorides are both established in rhenium chemistry. Clearly there is a high probability that osmium could be made to furnish similar compounds.

Chlorination of osmium metal by the halogen itself produces the tetrachloride, $OsCl_4$,[15] but introduction of a little oxygen into the chlorine stream causes the reaction to take place at a much lower temperature and changes the product to osmium oxytetrachloride, $OsOCl_4$. This compound bears a remarkable resemblance to the corresponding rhenium compound, $ReOCl_4$,[16] as shown by the properties of both summarized below.

Property	$ReOCl_4$	$OsOCl_4$
Colour of solid	Brown	Brown
Colour of vapour	Deep yellow	Deep yellow
m.p.	29°	32°
b.p.	223°	above 200°
Reaction with water	Hydrolyses; black ppt	Hydrolyses; black ppt
Organic solvents	Soluble	Soluble

Osmium oxytetrachloride is hydrolysed by water with the appearance of a black precipitate of hydrated osmium dioxide,

$$2OsOCl_4 + 4H_2O \rightarrow OsO_4 + OsO_2 + 8HCl.$$

With warm, dilute hydrochloric acid, on the other hand, an orange solution of tetrachloro-osmic acid results,

$$OsOCl_4 + H_2O \xrightarrow{HCl} H_2OsO_2Cl_4.$$

Starting with osmium metal, these reactions furnish a new and rapid synthesis of this acid and its salts. WINTREBERT,[3] starting from the tetroxide and proceeding through

[13] E. E. AYNSLEY, R. D. PEACOCK, and P. L. ROBINSON *J. Chem. Soc.* 1622 (1950).
[14] E. WEISE and W. KLEMM *Z. anorg. Chem.* **279**, 74 (1955).
[15] O. RUFF and F. BORNEMANN *Z. anorg. Chem.* **65**, 446 (1910).
[16] A. BRUKL and K. ZIEGLER, *Ber.* **65**, 916 (1932).

the complex nitrite, has succeeded in preparing the very soluble potassium and ammonium tetrachloro-osmates. The former of these was shown by HOARD[17] to have a tetragonal structure. Caesium tetrachloro-osmate(VI) is by contrast sparingly soluble in water and is isostructural with caesium hexachloro-osmate(IV), Cs_2OsCl_6, which possesses the cubic antifluorite structure. Such a difference in structure between a potassium and a caesium salt is not very common in this type of compound[18] and implies that in the potassium salt the $OsO_2Cl_4^{2-}$ groups are oriented in one direction, whilst in the caesium salt orientation is random.

The behaviour of osmium oxytetrachloride in cooled 10 N hydrochloric acid is quite different; it dissolves to form an intensely green solution from which the addition of caesium chloride precipitates a dark green salt. The green colour is fugitive, and keeping, diluting, or warming the solution causes it to change to the yellow-orange tetrachloro-osmic acid. Its lability has hindered any spectral or other investigation of the solution. However, an examination of the dark green caesium salt showed that it (1) contains more chlorine than is required for the formula $Cs_2OsO_2Cl_4$, (2) varies slightly in composition, and (3) has a cubic structure of the antifluorite type with a unit cell slightly larger than that of $Cs_2OsO_2Cl_4$ and increasing in size with increasing chlorine content. On the basis of this evidence, it is tentatively suggested, first, that the colour of the solution is due to the green ionic species $OsOCl_6^{2-}$ which results from the following reaction

$$OsOCl_4 + 2HCl \rightarrow H_2OsOCl_6,$$

and, secondly, that the caesium salt consists of $Cs_2OsO_2Cl_4$, though it is mixed with greater or lesser amounts of Cs_2OsOCl_6. An attempt to isolate pure Cs_2OsOCl_6 by conducting the reaction in cooled glacial acetic acid saturated with hydrogen chloride failed; only pure $Cs_2OsO_2Cl_4$ was obtained. SIDGWICK,[19] quoting I. and W. NODDACK, reports the preparation of the rhenium compound K_2ReOCl_6 by adding potassium chloride to what is described as the brown solution of $ReOCl_4$ in hydrochloric acid at $-10°$. This experiment has been repeated here, but in the first place $ReOCl_4$ did not give a brown colour even when the hydrochloric acid was cooled to $-40°$, a transient deep purple being all that was noticed; and, secondly, the addition of caesium chloride to the stable pale green solution which was formed gave an obviously heterogeneous mixture of white caesium perrhenate and pale yellow caesium hexachlororhenate(IV).

Osmium tetroxide is not attacked by fluorine at the ordinary temperature; actually, it is always formed during the fluorination of an osmium compound when moisture happens to be present; the fluorine then acts in its capacity as an oxidizing agent. However, when bromine trifluoride is used as a solvent and fluorinating agent, orange osmium trioxydifluoride, OsO_3F_2, has been isolated together with a series of complex oxyfluoride salts of the general formula $M^1OsO_3F_3$ (M^1 = K, Cs, Ag) to which it gives rise. Alternatively, the new oxyfluoride may be prepared by the direct fluorination of the metal in the presence of oxygen. It is unique among the volatile fluorine compounds of osmium in that it does not attack dry Pyrex glass

[17] J. L. HOARD and J. D. GRENKO *Z. Krist.* **87**, 100 (1934).
[18] Cf. WYCKOFF *Crystal Structures* Vol II. Interscience, New York.
[19] N. V. SIDGWICK *Chemical Elements and their Compounds* Vol. II p. 1302. Oxford University Press (1950).

and can be conveniently manipulated in an apparatus of this material. Moisture hydrolyses it rapidly,

$$OsO_3F_2 + H_2O \rightarrow OsO_4 + 2HF.$$

Osmium trioxydifluoride may be regarded as derived from osmium tetroxide by the replacement of one oxygen by two fluorine atoms. Surprisingly, it is much less volatile than the parent oxide. A point of interest is that in both its simple oxyhalides, $OsOCl_4$ and OsO_3F_2, osmium displays the unusual co-ordination number of 5.

The trifluoroperperosmates of which only the silver compound could be obtained pure, are orange salts, unaffected by dry air. Their solubilities in bromine trifluoride are in the reverse order of those found in the corresponding members of hexafluoro-osmate(V) series, [10] but are similar in this respect to those found by SHARPE[20] for the tetrafluoroaurates. Cold water dissolves them to form orange-yellow solutions which, on heating to just below the boiling-point, decolorise, liberating osmium tetroxide of which the liquid now smells strongly.

$$[OsO_3F_3]^- + H_2O = OsO_4 + 2HF + F^-.$$

The formation and behaviour of these salts are not unlike those of a corresponding series of compounds derived from Re(VII) which have been prepared by PEACOCK[21] and shown by him to have the general formula $M^1ReO_2F_4$ (M^1 = K, Rb, Cs, Ag).

MAGNETOCHEMISTRY OF Ru(VI) AND Os(VI)

The scanty literature on this subject is limited to the observations of MELLOR,[22] who found the complex nitrite $K_2[OsO_3(NO_2)_2]3H_2O$ to be diamagnetic, and those of DWYER and HOGARTH,[23] who found the complex $[Os(en\text{-}H)_4]I_2$, $3H_2O$ also to be diamagnetic. The character of these moments is surprising and in marked contrast to the paramagnetism expected for the presence of $2d_\epsilon$ electrons. The implication of the first of the measurements, as MELLOR pointed out, is open to question, since, the structure of the compound being unknown, the possibility of spin quenching by metal-metal interaction either directly, or through an oxygen bridge, cannot be ruled out.

On the other hand, the formulae $Cs_2RuO_2Cl_4$ and $Cs_2OsO_2Cl_4$ represent compounds of established structure in which the magnetic moment manifested might be expected to be a maximum one. In the event, both these compounds and also osmium oxytetrachloride were found to be diamagnetic, and it seems clear that the $2d_\epsilon$ electrons in Ru(VI) and Os(VI) compounds pair and cause the materials to be diamagnetic.

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[20] A. G. SHARPE *J. Chem. Soc.* 2901 (1949).
[21] R. D. PEACOCK *J. Chem. Soc.* 602 (1955).
[22] D. P. MELLOR *J. Proc. Roy. Soc. N.S.W.* **77**, 145 (1943).
[23] F. P. DWYER and J. W. HOGARTH *J. Amer. Chem. Soc.* **75**, 1008 (1953).

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ALUMINIUM CHLORIDE AS A SOLVO ACID AND FRIEDEL-CRAFTS CATALYST*

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Abstract—A detailed kinetic study has been made of the rate of chloride exchange between liquid phosgene and solute aluminium chloride. At low concentrations the rate is first order in aluminium chloride, but it changes over to a rate intermediate between 1 and 2 at higher concentrations. The cross-over point occurs at high concentration when the temperature is low and low concentration when the temperature is high. The energy of activation is 14·1 kilocalories in the first order region and 18·3 kilocalories in the region of higher order.

It is suggested that phosgene and aluminium chloride undergo a weak acid-base interaction leading to chloride exchange. It is also suggested that the cross-over to higher order is due to the appearance of ions in the solution, rather than to a specific chemical effect. In conformity to this picture, it is found that chloro-aluminate ions, for example, $AlCl_4^-$, undergo much slower exchange of chloride with solvent phosgene than does aluminium chloride. It is also found that the presence of ions in this solution can have a drastic effect toward raising the rate of exchange between phosgene and solute aluminium chloride.

Hydrogen chloride suppresses the rate of exchange of chloride between phosgene and solute aluminium chloride, possibly by means of such a reaction as

$$AlCl_3 + HCl + COCl_2 \rightleftarrows HCOCl_2^+ + AlCl_4^-$$

It appears that while there is no compound formation between hydrogen chloride and aluminium chloride by themselves, yet aluminium chloride can force hydrogen chloride to donate a proton to a proton acceptor, even one as weak as phosgene.

INTRODUCTION

A RATHER extensive study of the properties of phosgene solutions of aluminium chloride by GERMANN and co-workers[1] led to the first formulation of what has come to be called the solvent systems theory of acids and bases.[2] GERMANN observed that a solution of aluminium chloride in phosgene conducts much better than the pure solvent, evolves carbon monoxide on electrolysis or on reaction with alkali metals, and is capable of reacting with ionic chlorides to give conducting solutions. On the basis of these observations he constructed the following formulation: A parent solvent is a substance from which a system of solvo acids, solvo bases, and solvo salts is derived. A solvo acid is any electrolyte which, in a given parent solvent, yields cations identical with the cations of the self-ionization of the parent solvent, and in addition possesses atoms characteristic of the anion of the parent solvent. Thus sulphuric acid is a solvo acid in water, while hydrochloric acid is not. He considered aluminium chloride to be a solvo acid in phosgene by means of the process

$$Al_2Cl_6 + COCl_2 \rightleftarrows Co^{++} + Al_2Cl_8^{--}$$

* Presented at the Dallas Meeting of the American Chemical Society, April, 1956.
† Taken in major part from the Master of Science thesis of Mr. Lang.
[1] A. F. O. GERMANN and D. M. BIROSEL *J. Phys. Chem.* **29**, 1469, *et ante* (1925).
[2] T. MOELLER *Inorganic Chemistry*, Wiley, New York, p. 322ff. (1952).

A solvo base was similarly defined. A solvo salt can then be made by the reaction of a solvo acid with a metal or with a solvo base.

$$CO^{++} + Ca \rightarrow Ca^{++} + CO$$

$$CO^{++} + CaCl_2 \rightarrow Ca^{++} + COCl_2$$

As part of a recent investigation of the validity of the solvent system postulates[3] a tracer study was made of the phosgene-aluminium chloride system.[4] It was found, contrary to GERMANN's postulates, that the active agent in aluminium chloride solution was aluminium chloride itself, not CO^{++}. Calcium chloride transferred chloride ions directly to aluminium chloride when reacting with a solution of the latter. This work indicated a need for a detailed kinetic study of this system, which is reported in this paper, along with work pertaining to the nature of aluminium chloride as a Friedel-Crafts catalyst.

RESULTS AND DISCUSSION

$AlCl_3COCl_2$ exchange

Data from these experiments are summarized in Table 1 and in Fig. 1,[5] a log-log plot of rate of exchange of chloride between aluminium chloride and solvent phosgene. The small numbers to the right of the various straight lines are the slopes of these lines and, therefore, the order of exchange rate with respect to aluminium chloride. The most striking feature of the plots is, of course, the abrupt change in the order from about one to higher values. It will be observed that this change occurs at lowest concentration when the temperature is high and highest concentration when the temperature is low. Indeed, if the experiments had been performed at sufficiently low or sufficiently high temperatures, no such change in order could have been observed. The exchange process would have been either entirely first order or entirely of higher order. This observed change in order seems to be unique in the literature of exchange reactions. Probably the most thoroughly investigated exchange between a solute and a solvent of low dielectric constant is the chloride-catalysed exchange of thionyl chloride and solvent sulphur dioxide.[3c] In this case the exchange order is one with respect to thionyl chloride. And it appears, on the basis of more meagre data, that the order is also one with respect to acetyl chloride in acetic anhydride, acetic acid in acetic anhydride, and acetic anhydride in acetic acid.[3b] It does appear that the exchange between thionyl bromide and solvent sulphur dioxide is zero order with respect to the solute.[3a] But a change in order was observed in none of these cases.

[3a] R. E. JOHNSON, T. H. NORRIS, and J. L. HUSTON *J. Amer. Chem. Soc.* **73**, 3052 (1951).
[3b] E. A. EVANS, J. L. HUSTON, and T. H. NORRIS *J. Amer. Chem. Soc.* **74**, 4985 (1952).
[3c] B. J. MASTERS and T. H. NORRIS *J. Amer. Chem. Soc.* **77**, 1346 (1955).
[4] J. L. HUSTON *J. Inorg. Nucl. Chem.* **2**, 128 (1956).
[5] Equivalent fraction of aluminium chloride = (equivalents aluminium chloride) ÷ (equivalents aluminium chloride + equivalents phosgene). Equivalent fraction is used rather than mole fraction in order that concentration should be expressed in terms of the exchanging species, i.e. chloride. See G. FRIEDLANDER and J. W. KENNEDY (1955), *Nuclear and Radiochemistry*, Wiley, New York, p. 315 ff. for quantitative theory of exchange reactions.

Rate of exchange was calculated from the expression

$$R = \frac{0{\cdot}693(a)(b)}{T_{\frac{1}{2}}}$$

where a and b are the concentrations of aluminium chloride and phosgene. Values of $T_{\frac{1}{2}}$ were obtained from plots of log (l-fraction exchanged) versus time.

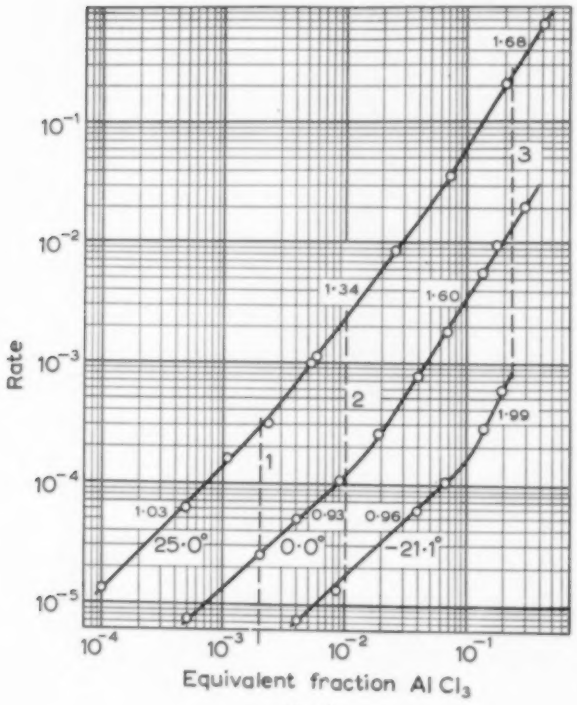
Rate
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
1·68
3
1·34
1·60
2
1·99
1
1·03
0·93
0·96
25·0°
0·0°
−21·1°
10^{-4}
10^{-3}
10^{-2}
10^{-1}
Equivalent fraction $AlCl_3$

FIG. 1.

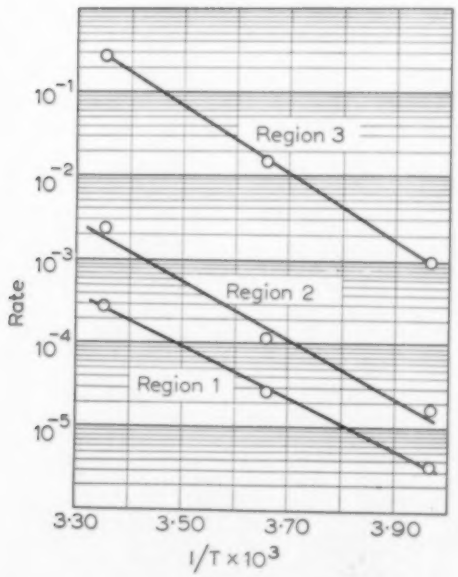
Rate
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
Region 3
Region 2
Region 1
3·30
3·50
3·70
3·90
$1/T \times 10^3$

FIG. 2.

TABLE 1.—PHOSGENE-ALUMINIUM CHLORIDE EXCHANGE

	Equivalent fraction	$T_{\frac{1}{2}}$	$R \times 10$	Slope
−21·1°	0·00423	405 hr	0·0721	0·96
	0·00865	460 hr	0·129	0·96
	0·0396	450 hr	0·586	0·96
	0·0663	420 hr	1·20	0·96
	0·136	285 hr	2·86	1·99
	0·194	185 hr	5·85	1·99
0°	0·000503	48·0 hr	0·0726	0·93
	0·00213	59·0 hr	0·250	0·93
	0·00419	58·0 hr	0·499	0·93
	0·00921	60·5 hr	1·045	0·93
	0·0192	52·0 hr	2·51	1·60
	0·0402	36·0 hr	7·42	1·60
	0·0694	25·0 hr	17·9	1·60
	0·132	14·5 hr	54·8	1·60
	0·173	10·5 hr	94·4	1·60
	0·300	7·5 hr	194	1·60
+25·0°	0·000098	5·20 hr	0·131	1·03
	0·000479	5·40 hr	0·616	1·03
	0·00109	4·70 hr	1·61	1·03
	0·00236	5·08 hr	3·20	1·03
	0·00532	3·70 hr	9·90	1·34
	0·00570	3·47 hr	11·3	1·34
	0·0265	2·13 hr	84·1	1·34
	0·0739	1·33 hr	358	1·68
	0·211	0·57 hr	2036	1·68
	0·417	0·26 hr	6546	1·68

Fig. 2 shows three plots for determination of activation energy, made at concentrations indicated in Fig. 1. It can be seen that good straight lines are obtained at regions 1 and 3 but not at region 2 which was deliberately chosen to include both first order and higher order plots. The fact that region 3 does give a good straight line indicates that a single exchange process is taking place in this region, and that the existence of orders intermediate between one and two is not to be ascribed to concurrent unimolecular and bimolecular processes involving aluminium chloride. It seems that the first order region corresponds at least approximately with the minimum of GERMANN's conductivity curves,[6] and thus the rising order at higher concentrations may be due to a greater population of ions in these regions, rather than to any specifically chemical effect. Perhaps the nature of the solutions in these regions of first order and higher order can be represented as

$$2AlCl_3 \rightleftarrows [AlCl_2^+, AlCl_4^-]$$

and

$$6AlCl_3 \rightleftarrows [Al_3Cl_8]^+ + [Al_3Cl_{10}]^-$$

[6] A. F. O. GERMANN *J. Phys. Chem.* **29**, 1148 (1925).

It may be noted that GERMANN's vapour pressure data indicate aluminium chloride to be partially dimerized in phosgene solution and these equations could as well have been formulated in terms of Al_2Cl_6.[7]

Phosgeno-aluminates

It has already been suggested[4] that solute aluminium chloride behaves toward solvent phosgene as a strong Lewis acid toward a slightly weaker one, the initial "neutralization" to form an aluminium chloride-phosgene complex being rapid, but the actual transfer of a chloride ion involving an appreciable activation energy. The kinetic data here reported are clearly compatible with this picture. In order to obtain collateral supporting evidence we have made a brief investigation of the exchange of chloride between solvent phosgene and chloro-aluminate ions, for example $AlCl_4^-$, $Al_2Cl_8^-$, etc. These ions may be regarded as aluminium chloride partially neutralized, and would be expected to exchange at a slower rate with the solvent than does aluminium chloride itself.

Table 2 summarizes data on the rate of exchange of solvent phosgene with chloro-aluminate and with mixtures of aluminium chloride and chloro-aluminate, the latter

TABLE 2

	Reactants	Phosgeno-aluminates		$T_{\frac{1}{2}}$ hr	
		Concentration $AlCl_3$	Concentration $AlCl_4^-$	Observed	$AlCl_3$ alone[a]
1	$AlCl_3^- + CaCl_2^-$	0	0·019	180	55
2	$AlCl_3^- + CaCl_2^-$	0	0·0398	190	37
3	$AlCl_3^- + CaCl_2$	0·0113	0·0063	59	54
4	$AlCl_3 + CaCl_2^-$	0·0104	0·0059	62	54
5	$AlCl_3^- + CaCl_2$	0·0160	0·0199	73	39
6	$AlCl_3 + CaCl_2^-$	0·0193	0·0209	72	37
7	$AlCl_3^- + NaCl^-$	0·0	0·0094	120[b]	59
8	$AlCl_3^- + NaCl^-$	0·0	0·0352	1520	40
9	$AlCl_3^- + NaCl$	0·0167	0·0201	39	37
10	$AlCl_3 + NaCl^-$	0·0169	0·0201	41	37

[a] That is, $T_{\frac{1}{2}}$ would have been this had no ionic chloride been added.
[b] Low because of incomplete reaction.

data taken from the previous paper.[4] The outstanding feature of these data is the great difference between the half-times reported in each case in the last two columns for runs 1, 2, 7 and 8. Clearly the chloro-aluminate ion, whatever its precise formula may be, is not nearly as active towards exchange with solvent phosgene as is aluminium chloride. And it is remarkable that there is so little difference between the last two columns for runs 2 and 4 and 9 and 10. In each of these cases approximately one-half of the aluminium chloride has been converted to the much less kinetically active chloro-aluminate ion, yet the half-time has been only slightly effected. And even in the cases of runs 5 and 6 the increase in half-time has been much less than one

[7] A. F. O. GERMANN and G. H. MCINTYRE *J. Phys. Chem.* **29**, 102 (1925).

might expect, considering that the aluminium chloride concentration is here in the region where the half-time is concentration-dependent (the order is greater than 1). It would seem that unreacted aluminium chloride is undergoing exchange more rapidly with the solvent in these solutions than it could if no ions had been present. Of course it is not surprising that in a solvent of such low dielectric constant as phosgene "ionic strength effects" should be very large. In any case, this may be taken as supporting evidence for the hypothesis previously offered to explain the change of order.

It may be noted that in the case of run 7 there was apparently incomplete reaction between sodium chloride and aluminium chloride. In this run (which had only a very small excess of sodium chloride over the stoichiometric quantity) the plot of log (1-fraction exchange) versus time underwent a sharp break at about 40% exchange and became almost flat. Runs 1, 2 and 8 gave good straight lines, and it may be assumed that there was substantially complete reaction in these three cases from the very beginning.

It is of interest that the unreacted calcium chloride and sodium chloride (solids) of runs 1 and 8 underwent at least appreciable heterogeneous exchange with the solution, the specific activity diminishing in each case by about 11%. No doubt this exchange was by chloride ions immediately adjacent to the surface of the solid. Since these solids were prepared in just the same way as the solids used in the previous work,[4] it is clear that the failure of solid ionic chlorides to undergo heterogeneous exchange with pure liquid phosgene (containing no solute) was not due to any lack of development of their surface area, but rather to the absence of ionic species in pure phosgene.

The great difference in rate between runs 2 and 8 may be due to a difference in solubility of calcium chloride and sodium chloride in phosgene. It is not unreasonable that solid sodium chloride should permit the higher concentration of chloride ions in phosgene and thus permit the equilibrium

$$Cl^- + AlCl_3 \rightleftarrows AlCl_4^-$$

to proceed further to the right. It may be asked whether we have any positive evidence that the formula of the chloro-aluminate ion is indeed $AlCl_4^-$ and not, for example $Al_2Cl_7^-$. In three runs the solutions were separated from unreacted solid ionic chlorides by decantation, and after removal of solvent phosgene the previously dissolved material was taken up in water for analysis. In all three cases the amount of chloride found was much closer to that expected for $AlCl_4^-$ than $Al_2Cl_7^-$; this does not of course preclude the existence of such ions as $Al_2Cl_8^-$ or other polymers of $AlCl_4^-$.[8]

$AlCl_3HCl$

It has been clearly shown that aluminium chloride and hydrogen chloride form no compound (e.g. $HAlCl_4$) of any substantial stability.[9] At temperatures as low as 120° no appreciable amount of hydrogen chloride is taken up by aluminium chloride, the conductivity of a saturated solution of aluminium chloride in liquid hydrogen

[8] See Experimental part for details.
[9a] H. C. Brown and H. Pearsall *J. Amer. Chem. Soc.* 73, 4681 (1951).
[9b] R. L. Richardson and S. W. Benson *J. Amer. Chem. Soc.* 73, 5096 (1951).
[10] M. Blau, W. T. Carnall, and J. E. Willard *J. Amer. Chem. Soc.* 74, 5762 (1952).

chloride is about the same as that of hydrogen chloride alone, and at higher temperatures the mixed gases show negligible deviation from ideality. However, such exchange experiments as have been done on this system,[10] have left room for feeble compound formation between the two substances. There was substantial *heterogenous* chloride exchange at 25° and even at −80°. Probably this heterogeneous exchange should be compared to the heterogeneous exchange between aluminium chloride and carbon tetrachloride,[11] there being of course not the slightest indication of any compound formation between these two substances.

Yet it is well known that hydrogen halides have a promoting action on aluminium halide operating as a Friedel-Craft catalyst. It has been found that aluminium chloride, which has no appreciable solubility in toluene, goes into solution in the presence of hydrogen chloride, apparently by means of the reversible reactions:[9a]

$$CH_3C_6H_5 + HCl + \tfrac{1}{2}Al_2Cl_6 \rightleftarrows [CH_3C_6H_6][AlCl_4^-]$$

$$CH_3C_6H_5 + HCl + \ Al_2Cl_6 \rightleftarrows [CH_3C_6H_6^+][Al_2Cl_7^-]$$

(Higher complexes presumably can also form).

BROWN and PEARSALL have suggested that it is such complexes which promote the solubility of aluminium halide catalyst and that these complexes play an important role in most Friedel-Craft reactions by furnishing a highly polar medium in which ionic intermediates may form and react. In other words, it might be stated that aluminium chloride can react with hydrogen chloride provided there is some place for the proton to go; some Brönsted base to accept it.

The phosgene-aluminium chloride system is formally similar to the system used by BROWN and PEARSALL, but phosgene certainly is a much weaker Brönsted base than toluene, and by using it we have a more drastic test of the ability of aluminium chloride and hydrogen chloride to react in the presence of a proton acceptor. Accordingly, we have done a few experiments to ascertain the effect of hydrogen chloride on the rate of exchange of chloride between aluminium chloride and solvent phosgene.

In Fig. 3 are plotted the ratio $T_{\frac{1}{2}}$ (HCl not present) ÷ $T_{\frac{1}{2}}$ (HCl present) as a function of the mole ratio of hydrogen chloride to aluminium chloride, concentrations of aluminium chloride being maintained as nearly constant as possible (equivalent fraction $\cong$ 0·038). The data have no precise numerical significance since we do not have the Henry's Law constants needed to calculate precisely the concentration of hydrogen chloride in the liquid phase,[12] but it is clear that hydrogen chloride suppresses the rate of exchange. Since aluminium chloride is, as we have seen, much more active kinetically toward exchange than chloroaluminate ion(s), it is probable that the mechanism of this suppression is a reversible equilibrium such as

$$AlCl_3 + HCl + COCl_2 \rightleftarrows HCOCl_2^+ + AlCl_4^-$$

Although definite compounds are formed in the toluene experiments of BROWN

[11] C. H. WALLACE and J. E. WILLARD *J. Amer. Chem. Soc.* **72**, 5275 (1950).

[12] One very rough estimation of a Henry's Law constant was made during the experiment which corresponds to the point near a mole ratio of 1·0 as explained in the experimental part. The data were used to correct the mole ratios plotted in Fig. 3.

and PEARSALL there is no evidence for any such formation here. This, of course, can be attributed to the weakness of phosgene as a Brönsted base. An attempt was made to calculate equilibrium quotients for the processes

(1) $$HCl + COCl_2 + AlCl_3 \rightleftarrows [HCOCl_2^+, AlCl_4^-]$$

(2) $$HCl + COCl_2 + 2AlCl_3 \rightleftarrows [HCOCl_2^+, Al_2Cl_7^-]$$

(3) $$HCl + COCl_2 + AlCl_3 \rightleftarrows HCOCl_2^+ + AlCl_4^-$$

by means of the assumption that the ratio (aluminium chloride converted to ions) ÷ (residual aluminium chloride) is the same as the half-time ratio. None of these equilibrium quotients showed satisfactory constancy. The one calculated for process

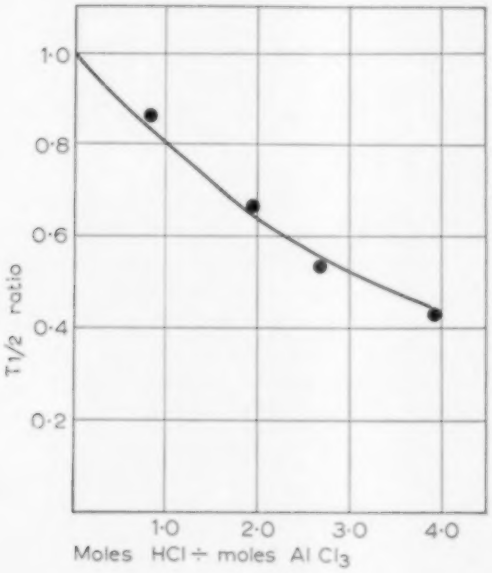

FIG. 3.

(3) showed the greatest deviation from constancy and certainly the degree of ionization in a solvent of so weak a dielectric constant can never be very substantial. More information on this system can be obtained by determining accurate Henry's Law constants for hydrogen chloride over solutions of aluminium chloride in phosgene, and such a study will be undertaken.

Experiments were also performed to ascertain whether the rate of exchange of chloride between hydrogen chloride and aluminium chloride, both dissolved in phosgene, could be measured. It turned out that the rate of exchange was immeasurably fast from 0° down to −60°, which was the lowest temperature at which a gas sample of suitable size could be obtained. At first it appeared that at 0° there was a measurable rate of exchange, of half-time approximately one minute, but the expected temperature dependence of this "half-time" failed to materialize, and it was, no doubt, a matter of equilibration between liquid phase and gas phase. It is clear then that the reversible equilibrium by which hydrogen chloride suppresses

the phosgene–aluminium chloride change is both very rapid and reversible. (The two gases can easily be pumped off, leaving pure aluminium chloride behind.) We consider that our results with phosgene to be one in accord with the results of BROWN and PEARSALL with toluene and constitute confirmation of their ideas.

Before concluding it might be well to discuss briefly a minor point left unsettled at the time of publication of the previous paper. It was observed[4] that when conventional plots were made of log (1-fraction exchange) versus time, the straight line did not intersect the zero-time ordinate at zero exchange. This was attributed to rapid exchange between aluminium chloride and hydrogen chloride impurity. It now appears that this effect is due rather to a small amount of radioactive hydrogen chloride produced by reaction of aluminium chloride with glass or with water adsorbed on glass, for it has not been possible to eliminate this effect by the most rigorous purification of the phosgene used. The effect has required the use of various modifications in the obtaining of data. At concentrations greater than 0·01, half-time values were obtained from the logarithmic plots and from the final specific activity of aluminium chloride, but at lower concentrations it was not possible to obtain satisfactory plots, because of this effect. Here, at the conclusion of a run, phosgene was fractionally distilled and only the least-volatile sample (presumed free of hydrogen chloride) was used for counting. Then a one-point plot was made to give a half-time value which was averaged with the value obtained from the specific activity of aluminium chloride to give the results reported. At the very lowest concentration (less than 0·0001) there was not sufficient aluminium chloride to give a sample of mercurous chloride large enough for counting, or indeed to permit an aluminium analysis. The half-time had to be obtained by comparison of the specific activity of phosgene (fractionally distilled) at some finite time with its infinite-time value. This latter value also served to furnish the aluminium chloride concentration. In this way we managed to investigate the exchange over a concentration range of a factor of 6000.

EXPERIMENTAL

Preparation of materials

These preparations differed materially from those previously described[4] only in one significant detail. Since it was desired to obtain phosgene as free of hydrogen chloride as possible, the following step was added to its purification. It was observed by EPHRAIM[13] that hydrogen chloride forms stable compounds with silver sulphate and with various other sulphates of transition metals. After it had been ascertained that silver sulphate underwent no appreciable reaction with phosgene (silver sulphate in a drying tube showed no appreciable gain in weight when phosgene was passed through it for several minutes) a column was constructed containing silver sulphate and a small amount of metallic antimony, the latter being present to remove chlorine impurity. After evacuation and heating the solids to de-gas, phosgene was passed through at the rate of about 2 litres per hour. Mass spectrometric analysis of the phosgene showed it to contain no more than 0·01% hydrogen chloride.

Frequently, in the course of this work, preparations of radioactive aluminium chloride were obtained with a distinct yellow colour. This yellow colour was due to some substance somewhat less volatile than aluminium chloride itself, and for some

[13] F. EPHRAIM *Ber.* **58**, 2262 (1925).

time was believed due to traces of iron in the aluminium metal used for the preparation. It now develops that this colour appears only when the glassware in which the preparation is made has been cleaned with chromic acid solution. If alcoholic potassium hydroxide is used as the cleaning solution this difficulty is avoided. Whatever the nature the coloured material may be, and its nature is quite obscure at the present time, it could be removed by distillation of the aluminium chloride over hot aluminium metal.

Procedure for making runs

Exchange experiments involving phosgene and solute aluminium chloride were usually performed in all-glass apparatus, fitted with breakoffs and seal points, though some of the earlier experiments were done in apparatus fitted with silicone-lubricated stopcocks. The general procedure has been described.[4] Those runs where calcium chloride or sodium chloride was added to the aluminium chloride solution were performed in all-glass apparatus. At the conclusion of each run the solution was separated from residual solid by decantation, phosgene was distilled away, the residue from the solution was taken up in water, and analyses were performed for aluminium and for chloride. The solid residue from the phosgene solution was determined simply by weighing. The analytical procedures otherwise used have been described in the previous paper. If the chloro-aluminate ion formed under these conditions is indeed $AlCl_4^-$, than we should expect the number of milli-equivalents of chloride present in phosgene solution to be 4/3 the number of milli-equivalents of aluminium. The 3 sets of data are as follows: chloride expected 0·0334; chloride found 0·0331. Chloride expected 0·460; chloride found 0·490. Chloride expected 0·801; chloride found 0·851. Better data could not be expected because the decantation afforded only a rough separation.

In the first of the series of runs where hydrogen chloride was added to the aluminium chloride solution, the experiment was performed in an apparatus where liquids and vapours were contained behind a stock valve. The apparatus permitted both investigation of the rate of exchange between hydrogen chloride and aluminium chloride and also of the suppression of the phosgene-aluminium chloride exchange by hydrogen chloride. A rough value of the distribution ratio of hydrogen chloride between liquid phosgene and the gas phase at 25° was obtained in the following manner: The total vapour pressure over the phosgene solution was balanced in one arm of the stock valve against a source of tank gas in the other arm, the pressure of this external gas being measured by an open-end mercury manometer. Using GERMANN's data[6] of the vapour pressure of phosgene at 25°, it was estimated that the ratio (millimoles phosgene per cc. liquid ÷ millimoles phosgene per cc. gas) = 150. This datum was used to correct the points plotted in Fig. 3 for the amount (5%–20%) of hydrogen chloride present in the gas phase.

Runs to measure the rate of low-temperature exchange between hydrogen chloride and aluminium chloride were performed in apparatus fitted with stopcocks. Runs to measure the suppression of phosgene-aluminium chloride exchange by HCl were performed in all-glass apparatus at 25°, the rate of exchange being calculated solely from the specific activity of aluminium chloride at the end of the run. It was felt that it would be useless to measure for this purpose the radioactivity in the gas phase, consisting as it did of two radioactive substances.

J. Inorg. Nucl. Chem., 1957, Vol. 4, pp. 40 to 47. Pergamon Press Ltd., London

CONDUCTIMETRIC STUDY OF THE REACTIONS BETWEEN METAL HALIDES AND LITHIUM ALUMINIUM HYDRIDE—I

ALUMINIUM CHLORIDE*

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(*Received* 21 *September* 1956)

Abstract—Conductivity curves are reported for the conductimetric titration of aluminium chloride by lithium aluminium hydride, and vice versa, in anhydrous ether solution. The formation and destruction of the substance $Al_2Cl_5^+AlH_4^-$ and of an ionized complex between lithium aluminium hydride and aluminium hydride are proposed to account for the maxima at intermediate stages in these curves. The titration of aluminium dichlorohydride, $AlHCl_2$, by lithium aluminium hydride follows a similar pattern, and a similar explanation is proposed. The conductivity of ethereal lithium aluminium hydride alone is very low.

THE reaction between lithium aluminium hydride (LAH) and aluminium chloride in ether solution is the most convenient method for preparing the relatively little-known substance aluminium hydride.[1, 2] Conductimetry appeared to be a promising technique for the detailed investigation of the reaction.[3]

EXPERIMENTAL

Part of the equipment and technique for the conductivity measurements has been described.[4] The necessity of protecting all solutions against traces of moisture, together with the general reactivity of the solutes, forced the development of a rather elaborate procedure,[5, 6] of which only the most significant features will be recounted here.

Anhydrous aluminium chloride (Eimer and Amend reagent grade) was weighed out in a dry box, transferred to a flask under dry nitrogen, and cooled in a solid carbon dioxide-acetone bath. Purified ether was added from a dropping funnel and the cooling bath was removed. This procedure resulted in solutions lighter in colour and more stable than those prepared with less drastic cooling. In the early part of the work, LAH (Metal Hydrides, Inc.) was used as received, but thereafter it was purified as follows: the crude material was refluxed overnight with ether, the solution was filtered[7] and evaporated to dryness (protected from moisture), and the residue was evacuated with a mechanical pump at 70–90° for 1½ to 2 hours, ground, and stored in a dry box. The product assayed 99% pure by hydrogen evolution, but even so it left a noticeable residue when redissolved in ether.

* Contribution No. 239 from the Department of Chemistry, Tufts University.

(1) A. E. FINHOLT, A. C. BOND JR., and H. I. SCHLESINGER *J. Amer. Chem. Soc.* **69**, 1199 (1947).

(2) E. WIBERG and M. SCHMIDT *Z. Naturforsch.* **6b**, 333 (1951).

(3) T. R. P. GIBB JR., M. D. BANUS, R. W. BRAGDON, and A. A. HINCKLEY, *Abstracts of Papers*, 119*th Meeting*, American Chemical Society, April 1951, p. 139P. The authors are indebted to Dr. GIBB for suggesting the problem, for making available to them the results of the early work, and for his frequent and valuable counsel.

(4) G. G. EVANS, T. R. P. GIBB JR., J. K. KENNEDY JR., and F. P. DEL GRECO *J. Amer. Chem. Soc.* **76**, 4861 (1954).

(5) J. K. KENNEDY JR. M.S. thesis, Tufts College (1953).

(6) F. P. DEL GRECO M.S. thesis, Tufts College (1954).

(7) The addition of dried Johns-Manville Celite Filter Aid (analytical grade) greatly facilitated the filtration of LAH solutions.

The solutions thus prepared were transferred through sintered-glass filters under pressure of dry nitrogen into their respective storage flasks; from here they were forced into burettes as needed and dispensed through separate lines of capillary tubing into the reaction vessel. Provision was made for rinsing the lines with pure dry solvent and for the withdrawal of samples for analysis.

For the handling of ethereal solutions, no completely satisfactory stopcock lubricant could be found, but two fluorocarbon greases proved tolerable. FCX-412[8] was used in the early part of the work; when this became unavailable, Fluorolube LG[9] took its place. The latter seemed more nearly inert chemically than the former, but it was also more readily dissolved by the ether.

Aluminium dichlorohydride etherate was prepared by Mr. GEORGE CHIZINSKY essentially as described by WIBERG,[10] by the mixing of aluminium hydride and aluminium chloride solutions in the theoretical ratio followed by distillation in high vacuum. In order to minimize decomposition, the temperature during distillation was not allowed to exceed 45°, although the process was thereby rendered extremely slow. The material had $d_4^{24.9}$ 1·123, n_D^{25} 1·4317.

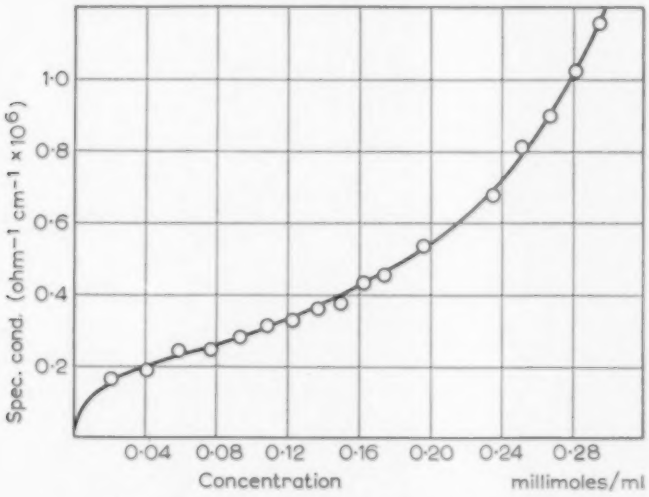

FIG. 1.—Conductivity of ethereal solutions of purified LAH.

RESULTS

The conductivity of ethereal solutions of aluminium chloride, alone and in the presence of lithium chloride, has been previously reported.[4] The addition of aluminium dichlorohydride, which is itself practically a nonconductor, appears to have little effect on the conductivity of aluminium chloride.

The curve of conductivity vs. concentration for purified LAH is shown in Fig. 1. Crude material gave a larger initial rise and less regular curves, but even then the specific conductance did not rise above 2×10^{-6} ohm^{-1} cm^{-1} for 0·25 M solutions. In the presence of lithium chloride, the curve lay slightly higher, but the increase was so small as to be of doubtful significance.

When a solution of aluminium chloride is titrated with LAH, the conductivity curves have the remarkable form typified by Fig. 2. The peak in conductivity appears at a point where about 17% of the equivalent[11] amount of LAH has been added

[8] E. I. duPont de Nemours and Co., Inc., "Kinetic" Chemicals Division.
[9] Hooker Electrochemical Company.
[10] E. WIBERG *Angew. Chem.* **65**, 22 (1953).
[11] Equivalence is calculated on the basis of the reaction $AlCl_3 + 3LiAlH_4 \rightarrow 4AlH_3 + 3LiCl$.

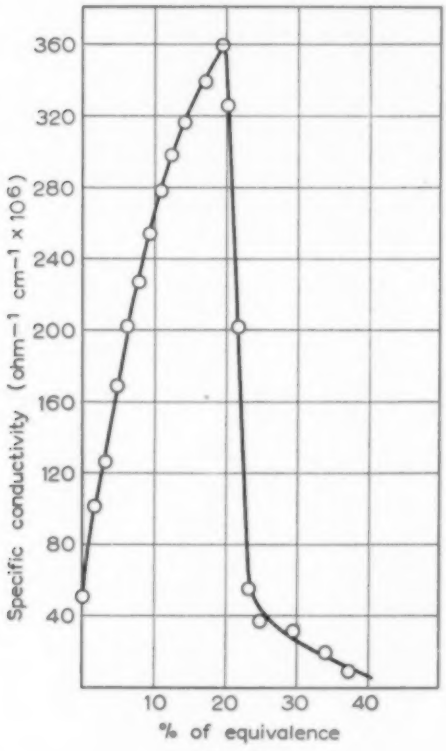

FIG. 2(a).

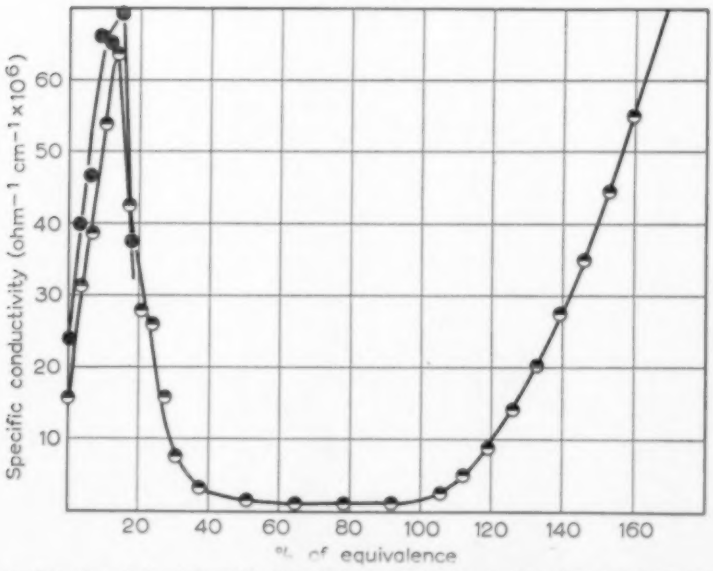

FIG. 2(b).—Titration of aluminium chloride solutions with LAH solutions. Initial concentration of $AlCl_3$: Curve *A*, ○, 0·340 millimoles per ml; curve *B*, ◓, 0·161; curve *C*, ●, 0·177 plus solid LiCl.

("17% of equivalence"). On the downward slope, between 20 and 50% of equivalence, the conductivity slowly drifts to lower values after each addition of LAH solution; in Fig. 2, the ordinates shown in that region are the lowest values attained.

It will be seen from curve *C* in Fig. 2 that the addition of suspended excess lithium chloride has a negligible effect on the shape and position of the maximum.

The results of the reverse titration, in which aluminium chloride is added to LAH, are shown in Fig. 3. Here the maximum conductivity is reached between 30 and 50% of equivalence.

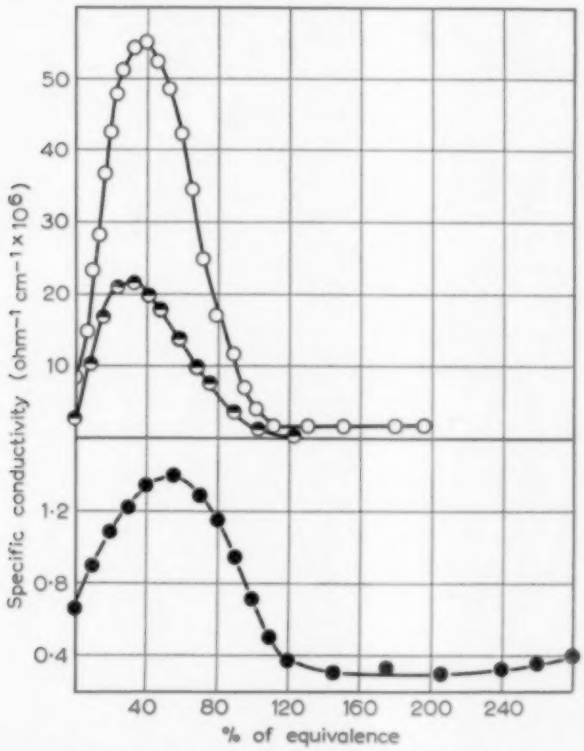

FIG. 3.—Titration of LAH solutions with aluminium chloride solutions. Initial concentrations of LAH: ○, 0·482 millimoles per ml; ◓, 0·383; ●, 0·139.

Especially significant results are obtained by titrating a solution of aluminium chloride with LAH solution to a point shortly beyond the maximum and then adding more aluminium chloride. Although the conductance is raised somewhat by this addition, it does not approach the value previously attained at the maximum (Fig. 4). When titration is resumed, the conductivity passes over a fresh maximum when the amount of new LAH reaches approximately 17% of the amount equivalent to the second portion of aluminium chloride.

Aluminium dichlorohydride reacts with LAH in ether solution to form a white precipitate which in all probability is lithium chloride, the reaction being $AlHCl_2 + 2LiAlH_4 \rightarrow 2LiCl + 3AlH_3$. Because of the small amounts of aluminium dichlorohydride available, the conductivity curves are less firmly established than those

obtained in other titrations, but it may be stated that the conductivity again passes through a maximum, this time located between 20 and 30% of equivalence (Fig. 5).

When mixtures of aluminium chloride and aluminium dichlorohydride are titrated

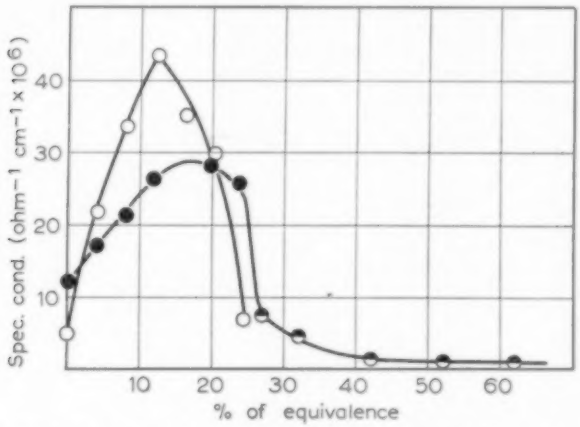

FIG. 4.—Titration of aluminium chloride solution with LAH solution (second portion of aluminium chloride added during titration). ○, titration of original aluminium chloride (initial concentration, 0·140 millimoles $AlCl_3$ per ml); ●, titration after addition of second portion (per cent of equivalence based on second portion only); ◓, continuation of ● but with per cent of equivalence based on total amount of aluminium chloride.

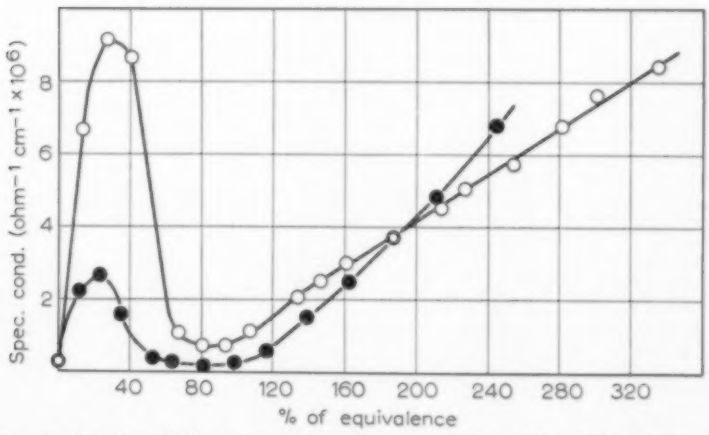

FIG. 5.—Titration of aluminium dichlorohydride solutions with LAH solutions. Initial concentrations of $AlHCl_2 \cdot (C_2H_5)_2O$: ○, 0·056 millimoles per ml; ●, 0·064. We do not know the reason for the discrepancy in the heights of the maxima.

with LAH, the conductivity passes through a single maximum, and there is no evidence of interaction between the chloride and dichlorohydride.

The addition of LAH to a freshly prepared, filtered solution of aluminium hydride results in conductances very much greater than those due to either solute alone, as shown in Fig. 6.

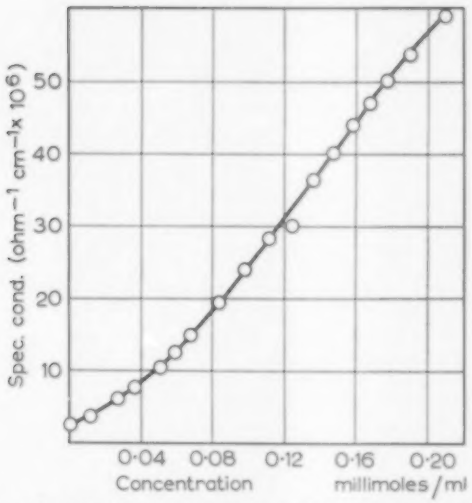

FIG. 6.—Conductivity of ethereal solutions of purified LAH in the presence of aluminium hydride. Abscissas denote concentration of LAH. Initial concentration of AlH_3: 0·398 millimoles per ml. Equimolarity of LAH and AlH_3 was not reached.

DISCUSSION

Before setting forth our deductions from the foregoing results, it is well to assess their reliability. First, the conductances of the solutions investigated are low by ordinary standards, and the presence of even small amounts of highly-conducting impurities could cause serious inconsistencies. Second, there is some uncertainty concerning the concentrations of the aluminium chloride solutions; analysis for aluminium (by 8-quinolinol) regularly indicated concentrations a few per cent higher than did analysis for chloride ion (by the Volhard method). Interaction between solute and solvent[4] may be responsible for this phenomenon; the formation of hydroxy aluminium chlorides[12, 13] by traces of water should still leave chloride ion in the solution, unless it took place before the solution was prepared. Third, although the temperature did not vary by more than 0·2° within any one run, the fact that different runs were carried out at temperatures ranging from 17 to 23° may have affected the reproducibility. And finally, in calculating the specific conductance at each point of the titrations, no account has been taken of the dilution caused by the addition of titrant. The available data show that the ordinary correction, which assumes proportionality between conductance and concentration, does not apply to these complicated systems (note the relative heights of the maxima in Fig. 3, and the corresponding initial concentrations of LAH); and in the absence of detailed knowledge of the conductance-concentration relationship, no trustworthy correction can be made.

The foregoing considerations make it plain that no great significance can be attached to our exact numerical conductance values. On the other hand, we have

[12] D. P. STEVENSON and O. BEECK *J. Amer. Chem. Soc.* **70**, 2890 (1948).
[13] J. R. BERCAW and A. B. GARRETT *ibid.* **78**, 1841 (1956).

found the shapes of the titration curves to be consistently reproducible and the conductances to be reproducible within a range of about 30%, except at the lowest values. This degree of consistency is an adequate basis for our conclusions.

In interpreting the data, we can immediately eliminate the hypothesis that ions produced by an equilibrium such as $AlCl_3 + LiCl \rightleftharpoons Li^+ + AlCl_4^-$ are responsible for the conductance at the maximum in Fig. 2. Such an equilibrium would account for the general shape of the curve, to be sure—the rising part would reflect the buildup of lithium chloride as the titration proceeded,[11] the falling part the depletion of aluminium chloride—but lithium and aluminium chlorides in ether solution do not give rise to such high conductivities.[4] Furthermore, the presence of lithium chloride at the beginning of the titration (Fig. 2, curve *C*) fails to change the shape of the curve.

Indeed, it is plain that no ionization equilibrium involving aluminium chloride can be responsible for the maxima under consideration. The curves of Fig. 4 show that the addition of more aluminium chloride does not reverse whatever process causes the downward slope of the conductance curve; furthermore, the behaviour of this second portion of chloride when titrated with LAH is unaffected by the presence of the products of the earlier titration.

The observed behaviour of aluminium dichlorohydride permits us to rule it out also as an intermediate in the titration of aluminium chloride.

We propose the following explanation of the data:

1. At 17% of equivalence, when there is one mole of LAH for every two moles of $AlCl_3$,[14] the reaction $LiAlH_4 + 2AlCl_3 \rightarrow LiCl + Al_2Cl_5^+ + AlH_4^-$ is complete, and conductivity is at a maximum.

2. The next step, the destruction of the ionic species, is complete at about 33% of equivalence, when there is (altogether) one mole of LAH for every mole of $AlCl_3$. The equation for this step is $LiAlH_4 + Al_2Cl_5^+ + AlH_4^- \rightarrow LiCl + 4\ AlH_2Cl$.

3. As the reaction proceeds to the equivalence point, the aluminium chlorohydride[10] formed in step 2 is destroyed: $LiAlH_4 + AlH_2Cl \rightarrow 2\ AlH_3 + LiCl$. The slow further drop in conductivity in this range may be due to this process, if the aluminium chlorohydride is slightly conducting in ether solution, or it may result simply from dilution of whatever conducting species are present.

4. The rise in conductivity beyond the equivalence point may be attributed to an interaction between LAH and aluminium hydride (cf. Fig. 6).

The same interaction will also account for the maximum of the curves in Fig. 3. In this case aluminium hydride is being formed in the presence of excess LAH, whereas beyond the equivalence point in Fig. 2 LAH is being added to aluminium hydride; furthermore, removal of LAH (by continuing the titration, Fig. 3) destroys the conductivity again. These facts justify the hypothesis that the interaction is an equilibrium. The curves of Fig. 3 have been less thoroughly studied than those of Fig. 2, however; the position of the maximum is not fully established, and the situation is complicated by the tendency of aluminium hydride to precipitate out of solution on standing; consequently, we are not prepared to propose a specific ionization process.

Beyond the equivalence point in the curves of Fig. 3, when the only substances present are presumably ether, aluminium hydride, lithium chloride, and excess aluminium chloride, the conductivity

[14] There has been surprisingly little work on the nature of ethereal solutions of aluminium chloride, but the recent results of BERCAW and GARRETT[12] appear to confirm the early conclusion of BECKMANN (*Z. physik. Chem.* **46**, 853 (1903)) that the aluminium chloride is in the monomeric ($AlCl_3$) form.

fails to rise even as much as would be expected for aluminium chloride-lithium chloride mixtures.[4] It appears that some sort of interaction is taking place between aluminium hydride and aluminium chloride, probably with the formation of the poorly-conducting chlorohydrides.

In the case of the titration of aluminium dichlorohydride with LAH (Fig. 5), we propose a mechanism analogous to that for aluminium chloride:

$$LiAlH_4 + 2AlHCl_2 \rightarrow LiCl + Al_2H_2Cl_3^+ + AlH_4^-;$$

$$Al_2H_2Cl_3^+ + AlH_4^- + 3LiAlH_4 \rightarrow 3LiCl + 6AlH_3.$$

According to this mechanism, the concentration of the ionic species reaches a maximum at 25% of equivalence, which is in agreement with the data. The ion $Al_2H_2Cl_3^+$ may be imagined to correspond to the ion $Al_2Cl_5^+$ postulated earlier, except that the bridge atoms are hydrogen instead of chlorine. The substance $Al_2H_2Cl_3^+ AlH_4^-$ here postulated has the same composition as the poorly-conducting AlH_2Cl of the other mechanism; we have not attempted to pursue the implications of this relationship.

Acknowledgement—The authors wish to express their appreciation of the support provided by the Office of Naval Research.

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CONDUCTIMETRIC STUDY OF THE REACTIONS BETWEEN METAL HALIDES AND LITHIUM ALUMINIUM HYDRIDE—II

ALUMINIUM IODIDE*

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(*Received* 21 *September* 1956)

Abstract—The conductimetric titration of aluminium iodide by lithium aluminium hydride, and vice versa, in anhydrous ether solution, furnishes curves superficially similar to those obtained when aluminium chloride is used. It is shown, however, that in the present case the data for the titration of the halide by the hydride are to be accounted for on the basis of the formation of an ionized complex (probably $Li^+Al_2I_7^-$) between lithium iodide and aluminium iodide. The reverse titration parallels the chloride experiments exactly. The conductivity of ethereal lithium iodide alone is very low.

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THE interesting changes in conductivity observed in the course of the reaction between aluminium chloride and lithium aluminium hydride (LAH) were reported in the first paper of this series.[1] The generality of this behaviour has now been investigated by extending the study to aluminium iodide.

The procedures have already been described. Anhydrous aluminium iodide was prepared by a modification of the method of PALMER and ELLIOT;[2] it was dissolved in dry ether by the same technique as had previously been used for the chloride. Anhydrous lithium iodide was prepared by a slight simplification of the method of BAXTER *et al.*[3]

RESULTS

One obvious difference between the present situation and the one previously reported[1] lies in the ether-solubility of the lithium iodide and the insolubility of the lithium chloride produced in the respective reactions. However, we have found that the conductivity of ethereal lithium iodide solutions is extremely low, as shown in Fig. 1, from which it is clear that, by itself, the compound will have a negligible effect on the conductivities observed. (The initial jump in the curve of Fig. 1 is probably due to the introduction of a trace of impurity along with the first portion of lithium iodide.)

The conductivities of ethereal solutions of aluminium iodide are plotted in Fig. 2. It will be noted that they are considerably higher than the conductivities of aluminium chloride solutions of corresponding concentrations.[4] Furthermore, the gradual addition of lithium iodide, itself a nonconductor, to such a solution increases the

* Contribution No. 240 from the Department of Chemistry, Tufts University.
[1] G. G. EVANS, J. K. KENNEDY JR., and F. P. DEL GRECO *J. Inorg. Nucl. Chem.* **4**, 40 (1957).
[2] K. J. PALMER and N. ELLIOT *J. Amer. Chem. Soc.* **60**, 1852 (1938).
[3] G. P. BAXTER, A. C. BOYLSTON, E. MUELLER, N. H. BLACK, and P. B. GOODE *ibid.* **33**, 901 (1911).
[4] G. G. EVANS, T. R. P. GIBB JR., J. K. KENNEDY JR., and F. P. DEL GRECO *ibid.* **76**, 4861 (1954).

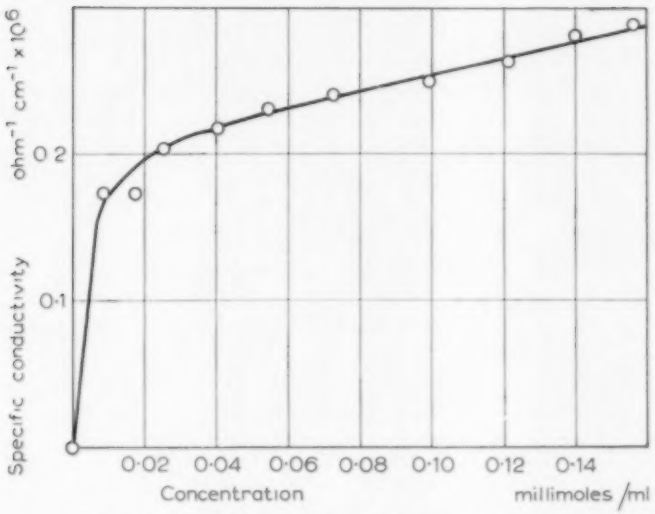

FIG. 1.—Conductivity of ethereal solutions of lithium iodide.

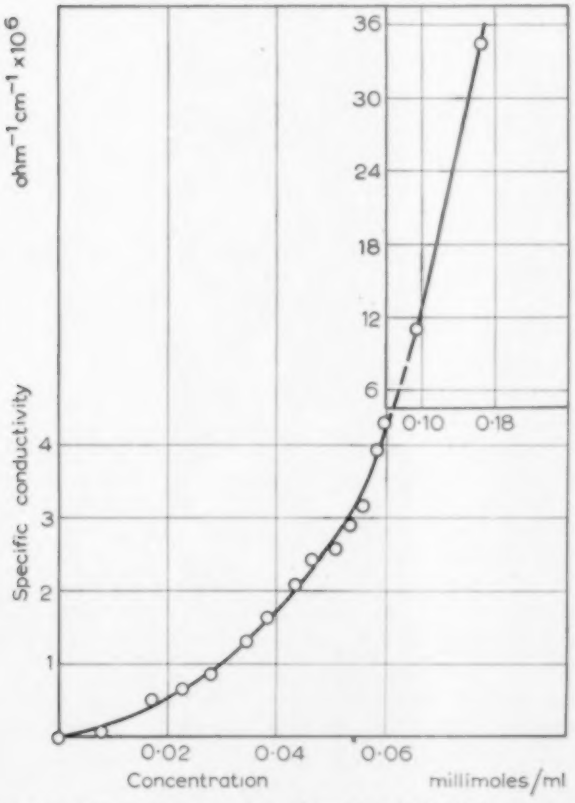

FIG. 2.—Conductivity of ethereal solutions of aluminium iodide (AlI_3). Points in the insert were obtained individually, not as part of the run which furnished the others.

conductivity more than tenfold, as shown in Fig. 3; attention is called to the levelling off of this curve at higher concentrations of lithium iodide.

When a solution of aluminium iodide is titrated with LAH, the conductivity curves have the form shown in Fig. 4, which bears a general resemblance to the aluminium chloride curves, but differs in detail. The conductivity reaches a maximum when 11% of the equivalent[5] amount of LAH has been added ("11% of equivalence"). From a point in the neighbourhood of 40% of equivalence almost to the equivalence point, the conductivity is practically constant and considerably lower than that of the original aluminium iodide solution; thereafter a slow rise sets in. The points on the downward slope of the curve do not show the drift noted in the aluminium chloride titrations. A fluffy white precipitate, which is believed to be the insoluble form of

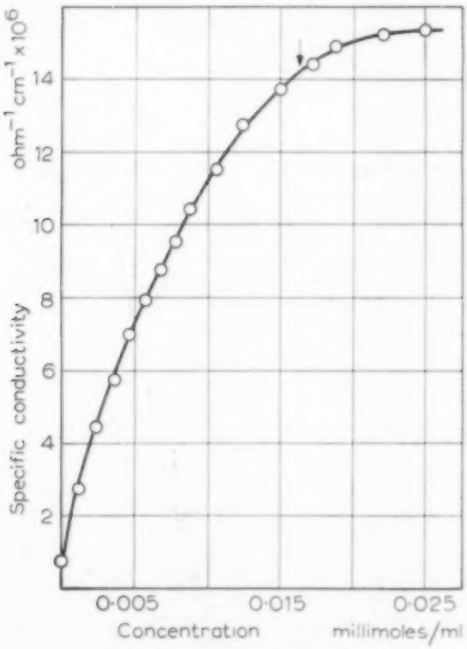

FIG. 3.—Conductivity of ethereal solutions of lithium iodide in the presence of aluminium iodide. Abscissæ denote concentration of lithium iodide. Initial concentration of AlI_3: 0·0417 millimoles per ml. Arrow marks point where solution contained 2 moles of AlI_3 for each mole of LiI.

aluminium hydride,[6] is formed in the course of the titration; no such material was observed during the aluminium chloride study, in which granular lithium chloride was formed.

The initial presence of lithium iodide greatly alters the first portions of these curves, as can be seen from Fig. 5. The conductivity in this case starts at a very high value and diminishes steadily (except for a small initial rise in one case, for which an explanation is proposed below). At 11% of equivalence, the conductivity has fallen

[5] Equivalence is calculated on the basis of the reaction $AlI_3 + 3LiAlH_4 \rightarrow 4AlH_3 + 3LiI$.
[6] A. E. FINHOLT, A. C. BOND JR., and H. I. SCHLESINGER *J. Amer. Chem. Soc.* **69**, 1199 (1947).

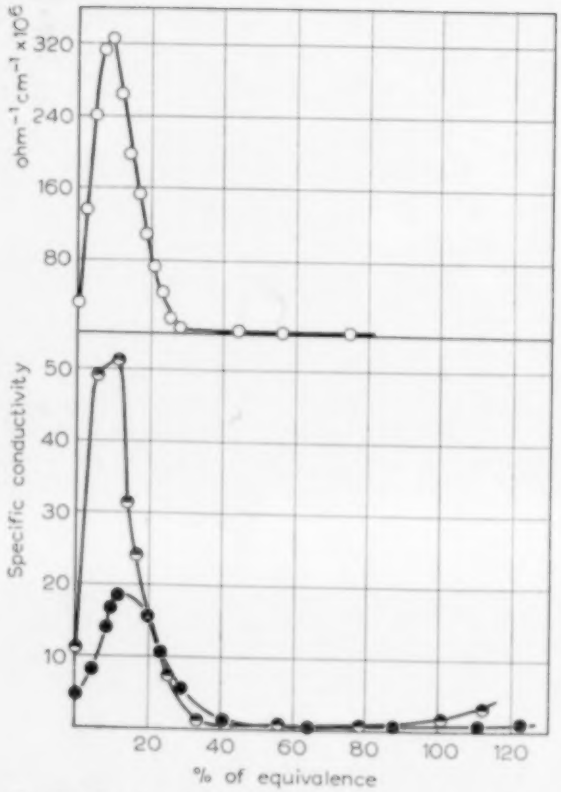

FIG. 4.—Titration of aluminium iodide solutions with LAH solutions. Initial concentrations of AlI_3: curve *A*, ○, 0·165 millimoles per ml; curve *B*, ◓, 0·094; curve *C*, ●, 0·059.

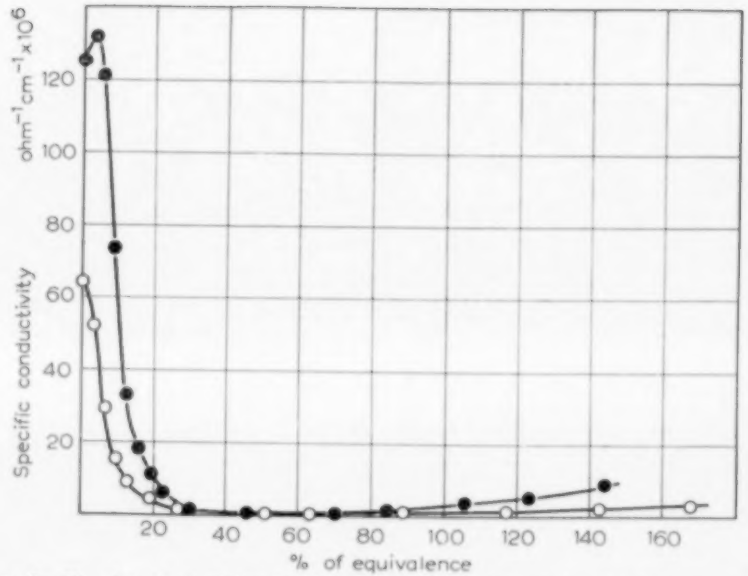

FIG. 5.—Titration of aluminium iodide solutions with LAH solutions in the presence of lithium iodide. Initial concentrations of AlI_3 and LiI respectively: curve *A*, ●, 0·082 and 0·109 millimoles per ml; curve *B*, ○, 0·045 and 0·191.

to a value comparable to that reached (as a maximum) in a titration without lithium iodide, and the two curves are closely similar thereafter.

Fig. 6 shows the curves for the reverse titration, in which an aluminium iodide solution is added to an LAH solution. The curves are not significantly different from

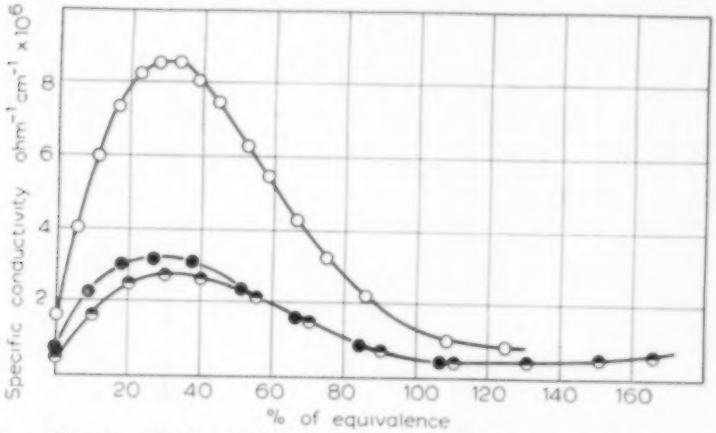

FIG. 6.—Titration of LAH solutions with aluminium iodide solutions. Initial concentrations of LAH: ○, 0·281 millimoles per ml; ●, 0·229; ◓, 0·164.

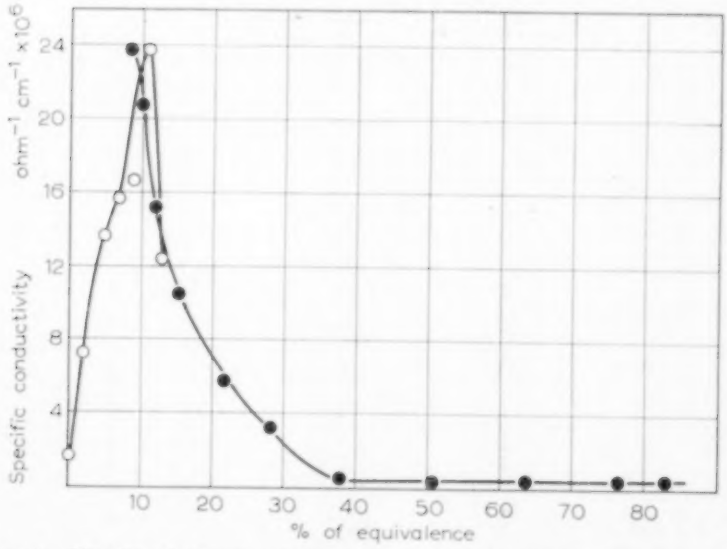

FIG. 7.—Titration of aluminium iodide solution with LAH solution (second portion of aluminium iodide added during titration). ○, titration of original aluminium iodide (initial concentration, 0·055 millimoles AlI_3 per ml); ●, titration after addition of second portion (abscissæ calculated on basis of total amount of aluminium iodide).

those obtained with aluminium chloride, and are undoubtedly to be interpreted in the same way.[1]

Finally, Fig. 7 shows the results obtained when titration of an aluminium iodide solution by LAH is interrupted by the addition of a second portion of aluminium

iodide. This figure has two significant features: (1) The additional aluminium iodide produces a conductivity equal to that attained at the maximum of the direct titration, even though the solution has been considerably diluted; and (2) the conductivity falls steadily when titration with LAH is resumed.

DISCUSSION

Despite the apparent similarity of Fig. 4 to the corresponding curves in the titration of aluminium chloride with LAH, the foregoing evidence points to a sharply contrasting explanation of at least the first part of the curve. An ionization equilibrium between aluminium and lithium iodides adequately accounts for the maximum observed in this case.

It is likely that aluminium iodide, like the chloride,[7] exists as the monomer in the presence of ether. The arrow in Fig. 3 indicates the point at which the molar ratio of AlI_3 to lithium iodide is 2 : 1, and from the fact that the curve levels off rather abruptly at this point one may tentatively conclude that the ionization process involves twice as many moles of one iodide as of the other and that it goes nearly to completion, so that excess lithium iodide can have little further effect. The equation provisionally adopted for the ionization process is

$$LiI + 2\,AlI_3 \rightleftharpoons Li^+ + Al_2I_7^-. \qquad (1)$$

The high initial conductivity of the curves of Fig. 5 is then due to the presence of ions formed by the above reaction.* LAH, when added, reduces the ionic concentration by reaction either with the ions themselves or with the AlI_3 in equilibrium with them. Since the conductivity has been reduced to a very low figure when the titration has reached approximately 33% of equivalence, we may suppose the removal of $Al_2I_7^-$ to be complete at this point. This implies the formation of an aluminium halohydride analogous to that postulated in the chloride case, the reaction being

$$2\,LiAlH_4 + Li^+ + Al_2I_7^- \rightarrow 3\,LiI + 4\,AlH_2I. \qquad (2)$$

The subsequent reaction is exactly analogous to the chloride process, viz.:

$$LiAlH_4 + AlH_2I \rightarrow LiI + 2\,AlH_3. \qquad (3)$$

When lithium iodide is initially absent, as in the curves of Fig. 4, the initial conductivity is relatively low; it rises as lithium iodide is formed in the course of the titration. At 11% of equivalence, the number of moles of lithium iodide formed is half the number of moles of aluminium iodide remaining, the two compounds are present in equivalent amounts according to (1), and the conductivity is at a maximum; the stoichiometry at this point is

$$LiAlH_4 + 3\,AlI_3 \rightarrow Li^+ + Al_2I_7^- + 2\,AlH_2I. \qquad (4)$$

Thereafter the process is described by equations (2) and (3).

[7] J. R. BERCAW and A. B. GARRETT *ibid.* **78**, 1841 (1956).

*It was noted that the conductivity of the mixtures of lithium iodide and aluminium iodide in ether when titration was begun was approximately twice what it had been 45 min earlier, immediately after mixing. This slow rise on standing, which presumably indicates that either reaction (1) or the dissolution of lithium iodide is a slow process, may have continued into the early part of the titration and outweighed the fall due to reaction with the first portions of LAH, thereby giving rise to the small maximum observed in curve *A* of Fig. 5.

The proposed mechanism is corroborated by a significant quantitative fact. At the maximum in curve *C* of Fig. 4, the concentrations of Li^+ and $Al_2I_7^-$, allowing for the slight dilution caused by the addition of titrant, are each 0·019 molar if equation (4) is correct. The observed specific conductivity is 18×10^{-6} ohm^{-1} cm^{-1}. Lithium iodide and aluminium iodide alone, at concentrations of 0·016 and 0·032 molar respectively (which means, if equation (1) goes practically to completion as we have inferred, that actually the concentrations of Li^+ and $Al_2I_7^-$ are 0·016 molar), give rise to a specific conductivity of 14×10^{-6} ohm^{-1} cm^{-1}—see the arrow in Fig. 3. Even if equation (1) is incorrect, the agreement still supports the conclusion that the lithium iodide-aluminium iodide combination is responsible for the conductivity at the maxima in Fig. 4.

It is evident that the data of Fig. 7 are also fully accounted for by the above hypothesis, with one possible exception: the additional aluminium iodide was sufficient to produce an appreciable excess of aluminium iodide over lithium iodide. This is a condition met with on the upward slope of the titration curve, and there should have been a small rise in conductivity when titration with LAH was resumed. We are not certain how this discrepancy should be explained, but we do not consider that it throws serious doubt on our conclusions.

The curves of Figs. 4 and 5 rise less rapidly beyond the equivalence point than do the corresponding curves in the chloride titrations. This phenomenon may result from the apparently greater tendency for aluminium hydride to precipitate out of a solution containing dissolved lithium iodide than out of one containing suspended lithium chloride, so that the amount remaining for ionized-complex formation is less.

Acknowledgement—The authors wish to express their appreciation of the support provided by the Office of Naval Research.

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A STUDY OF THE ELECTRON-EXCHANGE REACTION BETWEEN THALLIUM(I) AND THALLIUM(III) IN SULPHURIC ACID SOLUTIONS

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(*Received* 20 *July* 1956)

Abstract—Exchange between thallium(I) and (III) in 2·19 M sulphuric acid is about two-hundred times as fast as in perchloric acid solutions of the same ionic strength and hydrogen ion concentration. We have examined the rate of exchange in perchloric-sulphuric acid mixtures and in sulphuric acid-lithium sulphate mixtures. The experimental evidence shows that the rate can be predicted by several empirical rate equations. Some mechanisms, which lead to the rate equations, are discussed. We have also measured the rate of exchange as a function of sulphuric acid concentration and ionic strength, and as a function of temperature.

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INTRODUCTION

THE electron exchange reaction between thallium(I) and thallium(III) in perchloric acid solutions has been the subject of numerous papers and considerable discussion.[1–4] It appears that in perchloric acid the exchanging species are the thallium(I) ion and the hydroxothallium(III) ion and possibly the thallium(III) ion. The exchange in nitric acid has also been described[3] Recently CHALLENGER and MASTERS[5] have investigated the X-ray induced exchange between thallium (1) and (III) in 0·8 N sulphuric acid. The last study, as well as our own preliminary investigations, indicates that the exchange in sulphuric acid solutions is much more rapid than in perchloric acid solutions, but still proceeds with a measurable rate.

We undertook the present study to try to determine the reason for the acceleration of exchange in sulphuric acid and to see whether we might help clarify the thallium(I)-(III) exchange picture in general. Clarification of the role of sulphate ion has been a primary object of this work, in view of its surprising and seemingly anomalous effects on the thallium(I)-cerium(IV) reaction[6] and on the iron(II)-thallium(III) reaction.[7–9]

EXPERIMENTAL

Materials. Thallium(I) nitrate was obtained from E. H. Sargent and Co.; lithium carbonate, lithium sulphate, and sodium dichromate from Merk and Co., sodium cyanide from the Mallinckrodt Chemical Works; and all acids, except perchloric, used in these experiments were obtained from E. I. duPont de Nemours and Co., perchloric acid was from the J. T. Baker Chemical Company. The radioactive tracer used to follow the exchange was supplied by the Oak Ridge National Laboratory. 10 mc of Tl^{204} was shipped as the nitrate in 10 ml of 3 M nitric acid. The ammonium hydroxide and sodium hydroxide were Baker's reagent-grade chemicals.

[1] G. HARBOTTLE and R. W. DODSON *J. Amer. Chem. Soc.* **70**, 880 (1948); **73**, 2442 (1951).
[2] R. W. DODSON *J. Amer. Chem. Soc.* **75**, 1795 (1953).
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[7] A. J. BERRY *J. Chem. Soc.* **123**, 1109 (1923).
[8] C. E. JOHNSON JR. *J. Amer. Chem. Soc.* **74**, 959 (1952).
[9] O. L. FORCHHEIMER and R. P. EPPLE *ibid.* **74**, 5773 (1952).

Thallium(I) sulphate was prepared from recrystallized thallium(I) nitrate by treating it with an excess of sulphuric acid and evaporating the solution on a hot plate until fumes of sulphur trioxide appeared. To insure that all of the thallium was in the monovalent state, the solution was treated with sulphur dioxide and evaporated to fumes of sulphur trioxide a second time. The salt was recrystallized from distilled water until free of acid. Thallium(I) sulphate stock solutions were prepared with weighed amounts of this salt.

Thallium(III) sulphate solutions were prepared by dissolving thallium(III) oxide in sulphuric acid. The oxide was prepared by oxidation of thallium(I) sulphate solutions with potassium hexacyanoferrate(III) in 0·1 M sodium hydroxide. The oxide was washed free of hexacyanoferrate(II) and (III) ions by decanting the supernate and adding distilled water, which was then brought to the boiling-point and allowed to cool. The thallium(III) sulphate solutions were analysed for excess acid and both thallium(I) and (III) ions. Total thallium was found by reduction of the thallium(III) to thallium(I) and precipitation as the chromate (as described in standard analytical texts). The concentrations of the thallium(III) and hydrogen ions were determined in another sample by adding excess standard sodium hydroxide. The oxide thus precipitated, was washed several times, and the washings were combined with the supernate and were titrated with standard acid. The oxide was dried at 195°C for 1 hour and weighed. A correction was made for the amount of thallium(III) present in calculating the hydrogen ion concentration. The thallium(I) concentration was found by the difference in the two analyses and varied from 3 to 6% of the thallium(III) concentration. The hydrogen ion concentration was also determined by reducing the thallium with sulphur dioxide, heating the solution overnight on a steam bath to remove sulphur dioxide, and titrating with standard base, using phenolphthalein as an indicator. A correction was applied for the acid formed in the reduction.

Lithium perchlorate trihydrate was prepared from lithium carbonate by adding a slight excess of perchloric acid to lithium carbonate, evaporating to saturation, and cooling. The resulting solid was recrystallized from distilled water until free of acid and dried over a quantity of the salt which had been heated in an oven at 110°C.

The lithium sulphate was recrystallized and dehydrated at 200°C.

Standard sodium hydroxide solutions were prepared free of carbonate and standardized with potassium acid phthalate. Standard acids were analysed by comparison with the sodium hydroxide.

The sodium dichromate and sodium cyanide were used without further purification.

The radioactive thallium nitrate solution was converted to thallium(I) sulphate and a small amount of iron(III) scavenger was added. The solution was made basic with ammonium hydroxide and filtered. The solution was oxidized with hexacyanoferrate(III), filtered, and the oxide was washed, dried at 195°C, and weighed. The oxide (0·0649 g), obtained in this manner was treated with 10 ml of 1 : 1 sulphuric acid and diluted to 250 ml. This solution served as the stock of thallium(III) tracer.

A portion of this solution was added to inactive thallium(I) sulphate carrier after reduction with sulphur dioxide. A thallium(III) sulphate solution was prepared from this, as described previously. Analysis showed that the solution contained 0·080 M thallium(III) and 0·65 M hydrogen ion.

The molar ionic strength and molar concentrations of the sulphate, bisulphate, and hydrogen ions in the solutions used were calculated from data of SMITH[10] by a method described earlier by YOUNG and BLATZ[11] The solutions were made up from stock solutions already described.

Thallium(I) perchlorate was prepared by the addition of perchloric acid to thallium(I) hydroxide. Thallium(I) hydroxide was prepared from thallium(I) sulphate by titration with standard barium hydroxide, followed by evaporation of the solution and recrystallization. Thallium(III) perchlorate solutions were prepared and analysed in essentially the same manner as the sulphate solutions.

The exchange was carried out in solutions with molar ionic strengths of 3·68 [cf. PRESTWOOD and WAHL[3]], except for the series used to study the variation of rate with ionic strength. The concentrations of all solutions were 0·0100 M in thallium(I) and 0·0108 M in thallium(III), except for the series in which the dependence of the rate on thallium concentrations was studied. All reactions were carried out in 100-ml volumetric flasks.

Procedure. The exchange rate was measured in the following manner: After the concentration of the species to be used had been determined, the correct volume of the major acid was added to each

[10] H. M. SMITH Ph.D. thesis, University of Chicago (1949), and T. F. YOUNG *Record Chem. Progress* **12**, 81 (1951).
[11] T. F. YOUNG and L. A. BLATZ *Chem. Rev.* **44**, 98 (1949).

flask of a series. The thallium(III) and the thallium(I) solutions were added, followed by the minor acid and lithium salt, if present. The distilled water was added last and the flask was filled to a volume approximately 1 ml less than 100 ml and the flask was immersed in a water-bath set at 24·94 ± 0·01°. The flasks were allowed at least 3 hours to reach thermal equilibrium before the active thallium(III) sulphate was added.

Prior to starting a run, a number of (Whatman No. 540) 2·7-cm filter papers were dried for 1 hour at 110°C and weighed. A solution, prepared as described by HARBOTTLE and DODSON,[1] was used to separate the thallium(I) and (III). This was prepared and used in less than 24 hours. The solution was filtered just prior to use and was stored in an ice bath.

The active thallium(III) was added (1 ml in all cases). The addition was made, the volume adjusted, and the first shaking of the solution carried out in 15 sec. Zero time was taken as the time of the first shaking. Stirring was continued for 1 min. The first precipitation was made 2 or 3 min after the active thallium had been added. An aliquot (normally 5 ml) was removed from the flask with a pipette and added to twice its volume of precipitating solution. 10-ml samples were taken when the thallium(I) was 0·005 M. Separation time was taken as the midpoint of the 10-sec pipette drain time. The solution was swirled in an ice bath during the addition of the sample, to counteract the heat of neutralization. Since thallium(I) chromate is difficult to filter unless aged, the solution was allowed to stand for 5 min before filtration. The filtration was carried out in a steel funnel with with removable chimney. At the point of contact with the filter paper the chimney was 19 mm in diameter. The filter paper was placed on the support and the chimney on top. Filtration was aided by an aspirator, controlled by an arrangement for "bleeding in" air. In general, the precipitate was in contact with the supernate for less than 30 min. PRESTWOOD and WAHL[3] have shown that the heterogeneous exchange between the complexed thallium(III) species and the thallium(I) chromate precipitate is very slow and would be negligible under these conditions. After filtration, the sample was washed first with four 0·5-ml portions of precipitating solution, followed by four 0·5-ml portions of cold water. The sample was placed on a plate and a metal cylinder was placed on the sample to prevent curling, then dried at 110°C for 1 hour and weighed, mounted on cards, marked for centring of the sample, and counted. The washing procedure was tested on blank paper and was sufficient to give paper which had background count and zero weight of sample when only active thallium(III) chromate was present in the solution. Self-absorption is negligible in samples of the thickness used; all samples weighed about 12 mg. Filter papers averaged about 30 mg, and the weights of all papers from a given package were surprisingly uniform.

The sample was mounted directly in front of, and 2 cm from the 1-in. end window of a G-M tube. All samples were counted over an interval of time sufficiently long to obtain 10,000 counts. The dead times for the two G-M tubes used in this work were 2×10^{-4} and 4×10^{-4} sec. Coincidence and background corrections were made for each sample. Equilibrium specific activity was found by a precipitation made after ten half-lives had passed. Since the half-life of Tl^{204} is 3·5 (2·7) years, it was unnecessary to correct for radioactive decay.

Exchange half-times were then determined from graphs of log $(1 - F)$ vs. time (where F is the fraction exchanged). Each graph was drawn, using six to ten experimental points. Exchange rates and rate constants were calculated from the half-times and concentrations of thallium(I) and (III). These graphs gave excellent straight lines, but in multiple runs extreme values of the rate deviated from the average rate by as much as 10%.

RESULTS AND DISCUSSION

Variation of exchange rate with concentrations of thallium(I) and (III)

In order to determine whether or not the exchange is first-order in concentration of each of thallium(I) and (III), we have carried out the series of experiments which are summarized in Table 1. If a is the total thallium(I) concentration and b is the total thallium(III) concentration, then the rate of exchange R, divided by the product, ab, should be constant, provided that the exchange is actually first-order in thallium(I) and in thallium(III). We see that R/ab is constant within the limits of our experimental error, and thus we can conclude that in 2·19 M sulphuric acid, the rate of exchange

TABLE 1.—DEPENDENCE OF EXCHANGE RATE ON CONCENTRATIONS OF Tl^{I} AND Tl^{III} AT 25°. $\mu = 3{\cdot}68$; $(H^+) = 2{\cdot}90$; $(SO_4^{=}) = 0{\cdot}70$

Number of runs	(Tl^{I}) a (moles/l.)	(Tl^{III}) b (moles/l.)	R/ab (l./mole-min)
4	0·0100	0·0108	0·77
1	0·0100	0·0058	0·84
1	0·0100	0·0018	0·85
1	0·0050	0·0108	0·81
1	0·0010	0·0108	0·95
1	0·0050	0·0058	0·74
1	0·0200	0·0108	0·79

depends on the product of the first powers of the thallium(I) and (III) concentrations. We find, if $R = k(Tl^{I})^{\alpha}(Tl^{III})^{\beta}$, that $\alpha = 0{\cdot}98 \pm 0{\cdot}06$ and $\beta = 1{\cdot}00 \pm 0{\cdot}01$.

Variation of exchange rate with sulphate ion concentration at constant ionic strength

The values of R/ab which we observed for the exchange in 2·19 M sulphuric acid are about two hundred times those observed for the exchange in perchloric acid solutions of the same ionic strength (3·68) and hydrogen ion concentration. We have determined the rate of exchange in a series of solutions containing varying proportions of sulphuric and perchloric acids, but with the ionic strength and hydrogen ion concentrations held constant. These results are presented in Table 2. In Table 3 are shown the rates obtained from experiments carried out at constant ionic strength (also 3·68), in sulphuric acid-lithium sulphate mixtures. These reflect variation not only in sulphate ion concentration, but also in hydrogen ion concentration.

TABLE 2.—DEPENDENCE OF EXCHANGE RATE ON SULPHATE ION CONCENTRATION AT $\mu = 3{\cdot}68$, $(H^+) = 2{\cdot}90$, $(Tl^{I}) = 0{\cdot}0100$, $(Tl^{III}) = 0{\cdot}0108$

Number of runs	$(HClO_4)$ M	(H_2SO_4) M	$(LiClO_4)$ M	$(SO_4^{=})$ M	R/ab (expt.) (l./mole-min)	R/ab (ca'c).
4	0·000	2·19	0	0·70	0·77 ± 0·08	0·79
1	0·0001	2·19	0	0·70	0·77	0·79
1	0·0010	2·19	0	0·70	0·75	0·79
1	0·0100	2·19	0	0·70	0·73	0·79
1	0·100	2·12	0	0·69	0·71	0·77
1	0·500	1·80	0·130	0·59	0·59	0·60
1	1·00	1·43	0·243	0·47	0·41	0·40
2	1·50	1·06	0·380	0·35	0·25	0·25
1	2·00	0·679	0·490	0·23	0·15	0·14
1	2·50	0·294	0·620	0·10	0·057	0·055
1	2·89	0·000	0·720	0·007	0·0039	0·004
1	3·50*	0·000	0·110	0·007	0·0042	0·004

*$(H^+) = 3{\cdot}50$ M

TABLE 3.—DEPENDENCE OF EXCHANGE RATE ON HYDROGEN AND SULPHATE ION CONCENTRATIONS
$\mu = 3{\cdot}68$; $(Tl^{I}) = 0{\cdot}0100$; $(Tl^{III}) = 0{\cdot}0108$

Number of runs	(H_2SO_4) M	(Li_2SO_4) M	(H^+) M	$(SO_4^{=})$ M	R/ab (l./mole-min.)	R/ab (calc.)
4	2·19	0·000	2·90	0·70	0·77	0·79
1	1·94	0·167	2·50	0·77	0·88	0·92
1	1·60	0·386	2·00	0·83	0·96	1·04
2	1·28	0·574	1·56	0·88	1·08	7·13
1	0·852	0·805	1·00	0·99	1·40	1·36
1	0·652	0·944	0·750	1·07	1·75	1·67
1	0·404	1·021	0·450	1·10	1·94	1·91

We find that these data can be correlated with the experimental variables by means of one of the following equations:

$$R/ab = 0{\cdot}004 + 0{\cdot}41\,(SO_4^{=}) + 0{\cdot}93\,(SO_4^{=})^2 \tag{1}$$

$$R/ab = \frac{0{\cdot}134 + 9{\cdot}27\,(H^+)^2(SO_4^{=})^2 + 49{\cdot}8\,(SO_4^{=})^2}{[(H^+)^2 + K_1\,(H^+) + K_1K_2][1 + K_4(SO_4^{=})]} \tag{2}$$

$$R/ab = \frac{0{\cdot}0345 + 0{\cdot}7\,(H^+)^2(SO_4^{=}) + 12\,(H^+)^2(SO_4^{=})^3}{[(H^+)^2 + K_1(H^+) + K_1K_2 + K_3(SO_4)][1 + K_4(SO_4^{=})]} \tag{3}$$

Where,

$$K_1 = \frac{(TlOH^{++})(H^+)}{(Tl^{+3})}, \quad K_2 = \frac{(TlO^+)(H^+)}{(TlOH^{++})}$$

$$K_3 = \frac{(TlSO_4^+)}{(Tl^{+3})(SO_4^{=})} \qquad K_4 = \frac{(TlSO_4^-)}{(Tl^+)(SO_4^{=})}$$

and 0·004 is the value of R/ab, in the absence of sulphate ion, at $\mu = 3{\cdot}68$, $(H^+) = 2{\cdot}90$ M.

We feel that equation (1), which implies that the species of thallium(I) and thallium(III) do not change, even though considerable variation in $(SO_4^{=})$ and (H^+) occurs, is incompatible with the work of BELL and GEORGE[12] and of BIEDERMANN[13] on the sulphate complexing of thallium(I) and hydrolysis of thallium(III) respectively. For these reasons, we tend to discount the equation and mechanisms which lead to it.

Equation (2), which does not agree with experiment as well as (1) or (3), does not neglect complexing of thallium(I) or hydrolysis of thallium(III). The values of the K's required for the fit are, $K_1 = 6{\cdot}4$, $K_2 = 1$, $K_3 < 0{\cdot}05$ and $K_4 = 2$. Thus K_1 agrees with the value used by DODSON,[1,2] but it and K_2 do not coincide very well with BIEDERMANN's values. A value of $K_4 = 2$ is reasonable if we correct BELL and GEORGE's[12] infinite dilution value of 23 to ionic strength 3·68. However, MOELLER[14] indicates that K_3 should be large and the e.m.f. measurements of NOYES and GARNER[15] and

[12] R. P. BELL and J. H. B. GEORGE *Trans. Faraday Soc.* **49**, 619 (1953).
[13] G. BIEDERMANN *Arkiv. för Kemi* **5**, 441 (1953).
[14] T. MOELLER *J. Amer. Chem. Soc.* **75**, 4852 (1953).
[15] A. A. NOYES and C. S. GARNER *J. Amer. Chem. Soc.* **58**, 1270 (1936).

others suggest that $K_3 \cong K_4$. Thus we feel that 2 represents a better solution than 1, but its validity is also open to question.

Equation (3) predicts the data in Tables 2 and 3 very well, if we use BIEDERMANN's[13] values for the thallium(III) hydrolysis constants ($K_1 = 0{\cdot}077$, $K_2 = 0{\cdot}071$), the value $K_4 = 2$ (which is not inconsistent with the work of BELL and GEORGE[12]) and assume, as suggested by the work of NOYES and GARNER,[15] that $K_4 \cong K_3$, thus $K_3 = 2$.

It appears that we must disregard MOELLER's conclusions, but it seems, since they are based on pH of precipitation studies, that delayed precipitation effects could easily lead to erroneous conclusions.

We feel then that equation (3) represents the most reasonable solution. A combination of exchange processes such as

2. $^*TlSO_4^+ + Tl^+ \xrightarrow{k_1} TlSO_4^+ + {}^*Tl^+$

or

3. $^*Tl^{+3} + TlSO_4^- \xrightarrow{k_1} Tl^{+3} + {}^*TlSO_4^-$

and

4. $^*Tl(SO_4)_2^- + TlSO_4^- \xrightarrow{k_2} Tl(SO_4)_2^- + {}^*TlSO_4^-$

5. $^*Tl(SO_4)_3^{=} + Tl^+ \xrightarrow{k_2} Tl(SO_4)_3^{=} + {}^*Tl^+$

or

6. $^*TlSO_4^+ + Tl(SO_4)_2^{=} \xrightarrow{k_2} TlSO_4^+ + {}^*Tl(SO_4)_2^{=}$

(where *Tl is radioactive Tl^{204})

leads to

$$7.\quad R/ab = \frac{0{\cdot}0345 + k_1'(H^+)^2(SO_4^{=}) + k_2'(H^+)^2(SO_4^{=})^3}{[(H^+)^2 + K_1(H^+) + K_1K_2 + K_3(H^+)^2(SO_4^{=})][1 + K_4(SO_4^{=})]}$$

with k_1' and k_2' being composites of rate and equilibrium constants. If $k_1' = 0{\cdot}7$ and $k_2' = 12$, then this is equation (3).

Because the fairly rapid exchange rates may indicate reactions of oppositely charged species, we are inclined to favour 3 and 6.

In the Tables 2 and 3, we have listed the values of R/ab, calculated from equation (3), as well as the experimentally determined values. We notice that the calculated and experimental values agree within experimental error. A slight trend may be indicated in the Table 3 data, but since rather high sulphate ion concentrations obtain, the second thallium(III) sulphate complex may no longer be negligible.

Variation of exchange rate with concentration of sulphuric acid

We have also run a few experiments in which the exchange was measured in solutions containing varying amounts of sulphuric acid, in which the ionic strength was also permitted to vary, and the results are listed in Table 4.

We notice that the values of R/ab rise with falling sulphuric acid concentration and we have found that they rise more rapidly than is predicted by equations (1), (2), or (3). Thus it appears that the rate of reactions involved increases with decreasing ionic strength and this may suggest reactions involving oppositely charged species. However, in view of the complexity of the constants k_1' and k_2' and of the relatively high ionic strengths involved, such reasoning ought not be taken too seriously.

TABLE 4.—DEPENDENCE OF EXCHANGE RATE ON SULPHURIC ACID CONCENTRATION
$(Tl^{I}) = 0{\cdot}0100$, $(Tl^{III}) = 0{\cdot}0108$

Number of runs	(H_2SO_4) M	(H^+) M	(SO_4^{--}) M	μ	R/ab (l./mole-min)
1	2·38	3·16	0·79	4·06	0·78
4	2·19	2·90	0·70	3·68	0·77
1	1·53	2·00	0·46	2·55	1·00
1	1·21	1·56	0·35	2·00	1·08
1	0·36	0·45	0·10	0·65	1·25

Variation of exchange rate with temperature

We have measured the rates of exchange between 0·0100 M (Tl^{I}) and 0·0108 M (Tl^{III}) in 2·19 M sulphuric acid at three temperatures, and the results are shown in Table 5.

When we consider the evident complexity of the exchange and that the constants k_1' and k_2' are composites of rate and equilibrium constants, we do not believe that we should be justified in calculating an activation energy or entropy.

TABLE 5.—DEPENDENCE OF RATE OF EXCHANGE ON TEMPERATURE

Temperature (°C)	R/ab
0·0	0·0880
10·1	0·221
24·9	0·774

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ION-EXCHANGE STUDY OF THIOCYANATE COMPLEXES OF THE ACTINIDES AND LANTHANIDES

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Abstract—The ion-exchange behaviour of many tripositive actinides and lanthanides and yttrium from Dowex-1 anion-exchange resin with ammonium thiocyanate solutions has been studied. Lanthanides and yttrium elute sooner than actinides under all conditions studied. Neither lanthanides nor actinides showed a simple elution sequence of the members within the series. On elution from Dowex-50 with ammonium thiocyanate, the actinides eluted in the usual sequence of decreasing atomic number. The lanthanides studied also exhibited the usual elution sequence from Dowex-50; however, the actinides eluted sooner than the lanthanides of comparable ionic radius, indicating stronger complexing of actinides with thiocyanate.

INTRODUCTION

INTERESTING relationships have been observed between the lanthanide and actinide series upon elution from ion-exchange resin columns. With organic anion chelating eluants as ammonium citrate,[1-5] ammonium lactate,[5-9] and ammonium α-hydroxy-isobutyrate[10,11] both the lanthanides and actinides elute from Dowex-50 cation-exchange resin columns in order of decreasing hydrated ionic radii, which is the order of decreasing atomic number. The elution position of the actinides corresponds to the positions of lanthanides of comparable ionic radii, i.e. americium elutes near promethium.

With hydrochloric acid as eluant, a study[12] of the elution behaviour of tripositive plutonium, americium, curium, lanthanum, cerium, europium, ytterbium, and yttrium from Dowex-50 indicated an increasing dissimilarity in the behaviour of the lanthanides and actinides as the acid concentration was raised above 6 M. Both series eluted progressively earlier from 3 M to 6 M HCl; from 6 M to 13 M acid the lanthanide elution volume again increased, while the actinide elution volume continued the progressive decrease. This difference in behaviour of tripositive actinides and lanthanides was attributed to a greater degree of complex ion formation in the actinides, possibly due to 5-*f* orbital hybridization. In addition, a reversal of the

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elution order of the actinides was noted in strong acid. Extension of this work to include the actinides through fermium demonstrated the elution order to be fermium, einsteinium-californium (the two could not be resolved), berkelium, americium-plutonium, and curium in concentrated HCl,[5] and fermium, einsteinium, californium, curium, berkelium, and americium in concentration below 6 M acid.[13] With 13 M HCl as eluant from Dowex-1 anion resin,[5] the elution was that of increasing atomic number, which is the reverse of the Dowex-50 sequence, except for the americium-curium reversal.

DIAMOND[14] predicted on the basis of the *f*-orbital hybridization hypothesis that thiocyanate should complex more strongly with actinides than with lanthanides. Elution of europium much sooner than americium from Dowex-1 anion-exchange column with 4 M ammonium thiocyanate solution confirmed this prediction. It was felt that a detailed ion-exchange study of the behaviour of actinides and lanthanides with ammonium thiocyanate might shed light on the chemical differences between the two series.

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EXPERIMENTAL

1. *Equilibrium experiments*

The method used in these experiments consisted of equilibrating solutions of known ammonium thiocyanate concentration with weighed amounts of Dowex-1 anion resin initially in the chloride form. After the resin was converted to the thiocyanate form, tracer amounts of Am^{241} and $Eu^{154,155}$ were added. The mixture was stirred mechanically until no further change in the tracer-ion concentration occurred, at which time (approximately two hours) the system was considered to be at equilibrium. The Am^{241} content was determined by removing an aliquot of the solution, pipetting the aliquot on to a circular platinum plate, drying the plate under an infra-red heat lamp, igniting the plate to a dull red heat in a Meker burner flame, and then counting the alpha particles emitted by the Am^{241} in a 2π geometry alpha-particle counter. The $Eu^{154,155}$ mixture was determined in a similar manner, except that the beta particles emitted were detected by an end-window type Geiger-Müller counter. A thin absorber was placed between the sample and the Geiger-Müller counter to absorb the alpha particles emitted by the Am^{241}. The ammonium-thiocyanate concentration was determined by titration with a standard silver-nitrate solution.

The Dowex-1 resin was 8% cross-linked, 200- to 400-mesh, having an approximate capacity of 1·2 equivalents per litre of wet resin. Prior to use, the resin was washed alternately with hydrochloric acid, water, ammonium hydroxide, water, perchloric acid, water, hydrochloric acid. It was then oven-dried at 110°C overnight. Solutions were prepared from CP-grade ammonium thiocyanate and distilled water. pH was determined by indicator paper sensitive to changes of 0·2 of a pH unit. This method of determining pH was used because of the insensitivity of the system to pH (see below).

Measurements at other than room temperature were made by using a thermostated water-bath (±0·5°C) or an ice-bath.

Unless otherwise stated, all equilibrium experiments were performed in 15-ml centrifuge cones containing 0·500 g of resin and 5·00 ± 0·05 ml of solution.

2. *Ion-exchange resin column experiments*

The type of ion-exchange column employed was that described by THOMPSON *et al.*[5] It is essentially a glass tube of 2- to 3-mm diameter, which contains the resin bed, and an outer glass jacket through which vapour or liquid may be circulated for the purpose of temperature control. In these experiments trichloroethylene (b.p. 87°C) vapour or water from a thermostated bath was used to maintain constant temperature.

Resin for the Dowex-1 ion-exchange column bed was prepared from the 200- to 400-mesh stock by selecting that fraction which settled at a rate of ¼ to ½ cm min^{-1} in H_2O. During the course of the experiments the original supply of resin was exhausted. A new batch of Dowex-1 was obtained and

[13] G. R. CHOPPIN unpublished data.
[14] R. M. DIAMOND Ph.D. thesis, University of California Radiation Laboratory Unclassified Report UCRL-1434 (September 1951).

treated as described above. The fraction which settled at the rate of ¼ to ½ cm min^{-1} in 1 M HNO_3 was used, since it was found that this procedure gave a more uniform particle-size distribution. The Dowex-50 cationic resin was "wet-graded" to settle at the rate of ½ to 1 cm min^{-1} in water after treatment similar to that given the anion resin.

The pH of the NH_4SCN eluant was that of the solution as prepared. The pH of 0·5, 2·0, and 4·0 M NH_4SCN was 4·80, 4·48, and 4·21, respectively.

The Ce^{144}, Pm^{147}, Eu^{154}, Eu^{155}, and Y^{91} tracers were obtained from the Oak Ridge National Laboratory. The Gd^{148} had previously been produced by cyclotron bombardments. Tb^{160}, Tm^{170}, and Lu^{177} were produced by neutron irradiation of the stable element in the Materials Testing Reactor (Arco, Idaho). Dy^{165} and Ho^{166} were produced in the same manner in the University of California Livermore Reactor. Am^{241}, Cm^{242}, Bk^{249}, Cf^{250}, Cf^{252}, E^{253}, and Fm^{254} had been produced by neutron irradiation of Pu^{239}.

The resin bed was washed with the eluant for several hours at the temperature to be used during the elution. Known amounts of the tracer ions to be studied were combined in a centrifuge cone and evaporated to dryness in a water-bath. Then 30 to 60 μl of 4 M NH_4SCN were introduced into the cone and heated in the water-bath for a few minutes to dissolve the tracers. To ensure the reduction of plutonium to the III state, one μl of HI was added to the 4 M NH_4SCN. The eluant above the resin bed was removed and one drop of 4 M NH_4SCN was allowed to pass into the bed. Then the solution containing the tracers was passed into the bed and the elution was begun. The purpose in loading the tracers on the ion-exchange column in 4 M NH_4SCN was to ensure that the tracers were sorbed in a narrow band at the top of the resin bed.

The eluant was collected drop-wise on platinum plates, dried, ignited, and analyzed for the tracers by counting as described earlier. β^- emitters were detected by means of a Geiger counter. The one exception was Bk^{249}, whose soft β^- radiation was counted in a windowless proportional counter. Alpha-emitters were counted in a 2π geometry alpha-counter or in an alpha pulse-height analyzer, in which alpha-emitters may be identified by the characteristic energies of the alpha particles. This made possible resolution of overlapping peaks.

In order to get symmetrical elution peaks, the elution must be performed slowly enough to enable equilibrium conditions to be reached at all times. At 33°C it was necessary to maintain the eluant flow-rate to less than 0·15 ml per minute per cm^2 of resin bed cross-sectional area. At 87°C flow-rates of twice this value were satisfactory.

THEORETICAL

A theoretical analysis of the ion-exchange column process has been given by MAYER and THOMPKINS.[15] The relationship between the equilibrium absorption of an ion and its elution-peak position was shown to be as follows.

Define a quantity K_d as,

$$K_d = [M_r]/[M_s] \tag{1}$$

where $[M_r]$ and $[M_s]$ represent the concentration of an ion in the resin phase and solution phase, respectively, at equilibrium. K_d may be in any units desired, therefore,

$$K_d = M_r/M_s \text{ ml of solution/g of resin} \tag{2}$$

M_r/M_s now represents the distribution of the ion between resin and solution in one theoretical plate of the column, an analogy to a distillation column.

Finally,

$$C = K_d \times (\text{g of resin/ml of solution}) \tag{3}$$

where C represents the number of free-column volumes* which have passed through the resin bed when the ion is at its peak concentration in the eluate. The first free column volume is ignored in the calculation, since it provides no fractionation of the ions to be eluted.

* Free column volume is defined as the volume of solution in the resin bed.

[15] S. W. MAYER and E. R. THOMPKINS *J. Amer. Chem. Soc.* **69**, 2866 (1947).

RESULTS

Equilibration studies

The results of the equilibration experiments will be given in terms of the "K_d" defined by equation (2). Since only the solution phase is assayed for the tracer ion, the tracer ion present in the resin phase is obtained as the difference between the total amount of tracer ion present and that present in solution at equilibrium.

$$K_d = \frac{\text{c/m (total)} - \text{c/m (solution)}}{\text{c/m (solution)}} \times \frac{\text{ml of solution}}{\text{g of resin}} \qquad (4)$$

where c/m is the disintegration rate in counts/minute.

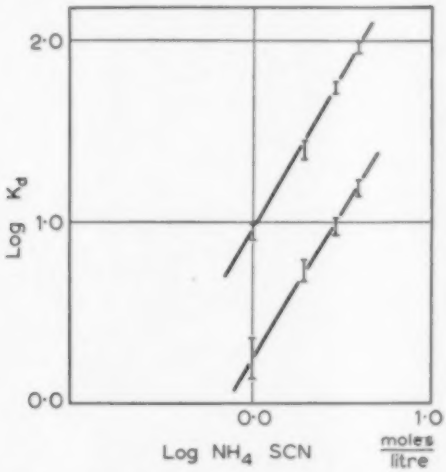

FIG. 1.—Logarithm of K_d vs. logarithm of ammonium thiocyanate concentration. Upper curve is for americium, lower is for europium.

In Fig. 1 the effect on K_d of varying ammonium thiocyanate concentration is given for americium and europium. The experiments were performed at room temperature and a pH of 3·5. The uncertainty of K_d is the statistical standard deviation error calculated from the number of counts recorded. If the ratio of K_d's at a given NH_4SCN concentration is taken as a rough measure of the tendency toward complex-ion formation, it can be seen that while both americium and europium are complexed strongly with SCN^-, the former is the more strongly complexed. It is assumed that only negatively-charged complexes are sorbed on the resin.

No appreciable effect on K_d was observed when the pH was varied from 2 to 5 in both 1 and 3 M NH_4SCN. This is the expected behaviour of a strong acid such as HSCN ($K_a = 0{\cdot}14$).[16]

The effect of temperature on the K_d of americium and europium at a pH of 3·5 is shown in Fig. 2, where log K_d is plotted vs. the reciprocal of the absolute temperature. While both americium and europium show an appreciable temperature-dependence, the europium-dependence is not as great.

[16] T. SUZUKI and H. HAGISAWA *Bull. Inst. Phys. Chem. Research (Tokyo)* **21**, 601 (1942).

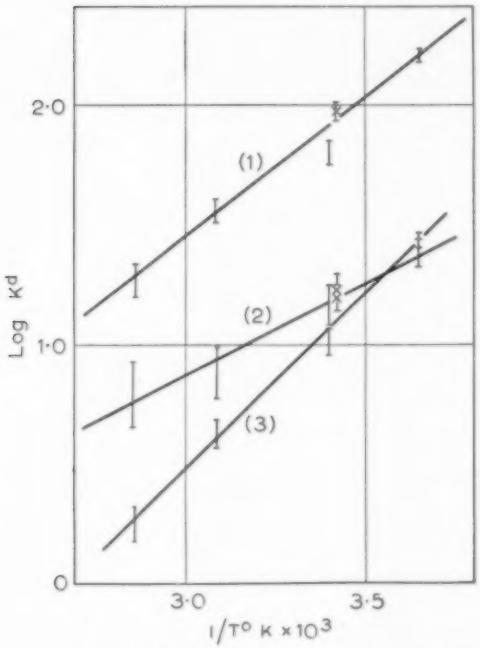

FIG. 2.—Variation of logarithm of americium and europium K_d's with temperature. Curve 1 is for 3 M NH_4SCN and americium; curve 3 for 1 M NH_4SCN and americium; curve 2 for 1 M NH_4SCN and europium. "X" indicates measurements one month after initial experiment.

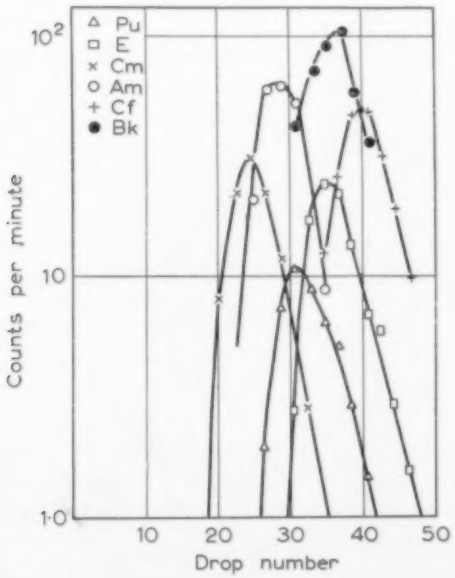

FIG. 3.—Elution of actinides from Dowex-1 with 2 M ammonium thiocyanate at 87°C.

Elution studies

The conditions (ammonium thiocyanate concentration, temperature, size of resin bed) necessary to elute the tracers at a convenient eluate volume were selected with the aid of equation (3) and the equilibration data. For this system, equation (3) becomes,

$$C = K_d \times 0{\cdot}9 \qquad (3a)$$

Table 1 shows the agreement between equilibration and column data for americium under various conditions.

TABLE 1.—COMPARISON OF EQUILIBRATION AND COLUMN DATA FOR AMERICIUM

$[NH_4SCN]$ moles/litre	Temperature (°C)	Resin-bed dimensions Diameter (mm)	Length (cm)	Resin batch	K_d (Am) equilibration	column
2·0	~25	2	14	1	~35	30
0·5	~25	3	4	1	~3	2
2·2	33	2	10·5	1	30	24
2·2	87	2	10·5	1	8	6·4
1·1	87	2	10·5	1	1·8	1·5
1·0	33	2	6·5	2	9	10
2·0	87	2	5·9	2	6·6	8
0·96	87	3	5·6	2	1·4	1·0

A typical elution curve for the actinides from Dowex-1 is given in Fig. 3. This particular elution was performed at 87°C with 2 M NH_4SCN as eluant and a resin bed 2 mm × 6 cm. The results of other experiments on the actinides are summarized in Table 2 after subtraction of one free column volume.

In Table 3 the results of the lanthanide elutions from Dowex-1 are presented after subtraction of one free column volume. All runs were performed on a 3 mm × 6·5-cm resin bed, using 2·0 M NH_4SCN as eluant at a temperature of 33°C. It was not

TABLE 2.—ACTINIDE ELUTION PEAK POSITIONS FROM DOWEX-1

NH_4SCN (M)	T (°C)	Resin-bed dimensions Diameter (mm)	Length (cm)	Resin batch No.	Drop No. to peak Pu	Am	Cm	Bk	Cf	E	Fm
2·0	~25	2	14	1		230	210				
0·5	~25	3	4	1		9	8				
0·55	~25	3	4	2		11	10				
2·2	33	2	10	1	136	121	109				
1·0	33	2	7	2	40	37	33	60	67	57	
2·2	87	2	10	1	35	35	32				
1·1	87	2	10	1	8	8	7				
2·0	87	2	6	2	30	28	24	36	41	35	
0·96	87	2	6	2			3	5	6		
0·96	87	3	6	2			5		11	9	
0·96	87	3	6	2		6	5		11	8	10

possible to determine elution positions for all the lanthanides studied in a single experiment because of the difficulty of resolving complex mixtures of β emitters. A series of experiments under identical conditions was performed. As the elution volume of a given lanthanide varied somewhat between experiments, it was necessary to "normalize" the various experiments before a relative comparison of individual

TABLE 3.—LANTHANIDE ELUTION PEAK POSITIONS FROM DOWEX-1

Experiment	Drop No. to peak									
	Ce	Pm	Eu	Gd	Tb	Dy	Ho	Tm	Lu	Y
1	12	21	26	—	—	—	—	—	—	—
2	14	21	26	—	—	—	—	23	—	17
5	—	20	—	24	—	23	22	—	—	—
6	12	20	—	—	—	23	22	—	—	—
7	13	18	—	24	—	—	22	—	—	—
8	11	20	—	—	25	—	—	—	—	—
11	10	20	—	—	—	—	—	24	—	—
12	11	—	26	24	26	—	—	—	—	—
13	13	—	27	24	26	—	—	—	—	—
15	—	—	26	24	—	—	—	—	—	—
17	—	20	—	—	—	—	—	—	26	—
18	11	20	—	—	—	—	—	—	30	—

TABLE 4.—ACTINIDE AND LANTHANIDE ELUTION PEAK POSITIONS FROM DOWEX-1

Expt. No.	NH_4SCN (M)	T (°C)	Resin-bed dimensions		Drop No. to peak							
			Diameter (mm)	Length (cm)	Ce	Pm	Eu	Tm	Lu	Y	Am	Cm
1	0·5	~25	3	4	—	—	1 ± 1	—	1 ± 1	—	9	8
2	2·0	~25	2	15·5	17	—	—	—	—	28	260	—
3	2·2	33	2	10	—	14	—	15	—	12	121	109
4	2·5	87	2	10	8	—	—	—	20	—	53	47

lanthanides could be made. Gadolinium, europium, or promethium was used as a base for normalization.

Where it was possible (e.g. with promethium) β-emitter peaks were resolved by interposing an absorber which would reduce the radiation of one of the nuclides to a very low level. If one of two lanthanides which eluted close together had a conveniently short half-life, the peak was resolvable. The combined peak was counted upon elution, then re-counted after a time sufficient for the short-lived component to become insignificant. The short-lived component is then obtained by difference.

Table 4 presents the results of some experiments in which both actinides and lanthanides were present. Again one free column volume has been subtracted. Only resin from the first batch was used.

It is interesting to compare the results of Table 4 with those predicted from the

equilibration data. It is assumed that the relative elution positions of the lanthanides are approximately independent of temperature and M of NH_4SCN, as are those of actinides. From the data in Table 3, the europium peak position should be drop 18

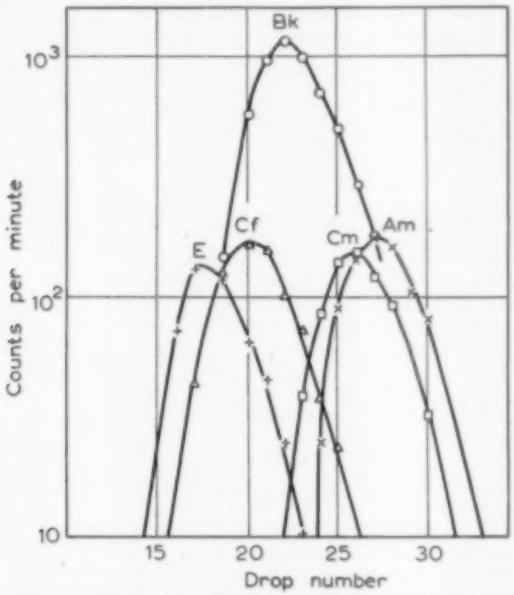

FIG. 4.—Elution of actinides from Dowex-50. Resin bed 2 mm diameter × 5 cm length. 1·8 M ammonium thiocyanate eluant. 87°C.

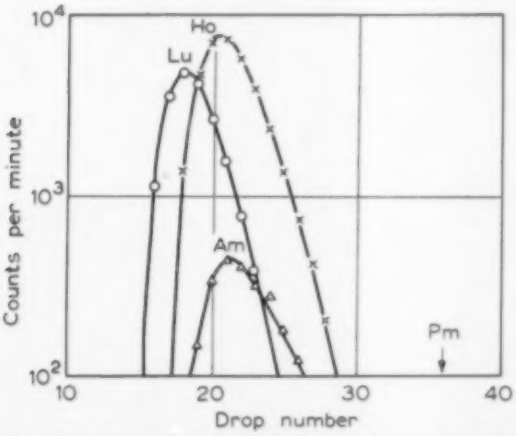

FIG. 5.—Elution of lutetium, holmium, promethium, and americium from Dowex-50. Resin bed 2 mm diameter × 5 cm length. 2·0 M ammonium thiocyanate eluant. 87°C.

for both experiments 3 and 4 in Table 4. As the drop number to peak for an ion is directly proportional to its K_d, for experiments 3 and 4 the ratio of K_d (Am) to K_d (Eu) is 6·7 and 2·9 respectively. From the equilibration data the ratios should be 5 and 3·2. This agreement is considered to be satisfactory.

The actinide behaviour on elution from Dowex-50 is shown in Fig. 4. This

experiment was performed at 87°C with 1·8 M NH_4SCN as eluant. The column bed was 2 mm by 4 cm packed with Dowex-50 4% cross-linked resin. The elution order is just the order of decreasing atomic number. Furthermore, curium still preceded americium, using 4·4 M NH_4SCN as eluant.

Fig. 5 shows the behaviour of americium compared to lutetium, holmium, and promethium. Conditions were the same as above, except that the eluant was 2·0 M NH_4SCN. The promethium position was obtained in separate experiments and is indicated by an arrow.

DISCUSSION

The linearity of the data plotted in Fig. 1 is due to the fact that only a limited range of SCN-concentration was investigated. Consider the reactions involved in the case of americium. First, the formation of the negatively-charged complex,

$$Am^{+3} + xSCN^- = Am(SCN)^{3-x} \tag{5}$$

$$K_1 = (Am(SCN)_x^{3-x})/(SCN^-)^x(Am^{+3}) \tag{5a}$$

Then the sorption on the resin of the complex ion,

$$Am(SCN)_x^{3-x} + yRSCN = R_yAm(SCN)_x + ySCN^- \tag{6}$$

$$K_2 = \frac{(R_yAm(SCN)_x)(SCN^-)^y}{(RSCN)^y(Am(SCN)_x^{3-x})} \tag{6a}$$

Since the americium is in tracer concentration, no problem arises in evaluating the "(RSCN)" term, $(R_yAm(SCN)_x \ll (RSCN)$, so that (RSCN) is constant and is arbitrarily set equal to unity. Assume for simplicity that concentrations may be substituted for thermodynamic activities. Recalling equation (1),

$$K_d = \frac{[Am_{(r)}]}{[Am_{(s)}]} = \frac{[R_yAm(SCN)_x]}{[Am^{+3}] + [Am(SCN)_x^{3-x}]} \tag{7}$$

Substituting from (5a) and (6a) in terms of (SCN^-), K_1, and K_2; after simplification, (7) becomes

$$K_d = \frac{K_1K_2[SCN^-]^{x-y}}{1 + K_1[SCN^-]^x} \tag{8}$$

Inspection of equation (6) shows that in order to preserve electrical neutrality in the resin, $x - y = 3$. Making this substitution and taking logarithms,

$$\log K_d = \log K_1K_2 + 3 \log [SCN^-] - \log (1 + K_1[SCN^-]^x) \tag{9}$$

Obviously, a plot of $\log K_d$ vs. $\log [SCN^-]$ is not linear. The actual situation could be further complicated, since it is possible that more than one species of negatively charged complex ion may exist and sorb on the resin. It is worth noting that when essentially all of the americium is complexed, the third term on the right in equation (9) becomes "$\log K_1[SCN^-]^x$."

Making this substitution and taking the derivative,

$$\frac{d \log K_d}{d \log [SCN^-]} = 3 - x \tag{10}$$

This, of course, predicts a linear plot with *negative* slope numerically equal to the charge on the americium thiocyanate complex ion.

It can be seen from Fig. 6 that neither the actinide nor lanthanide elution positions fall in a simple order of atomic number from Dowex-1 with NH_4SCN, as is the case in elution from Dowex-50 with most eluants (the only exception is the plutonium-americium-curium "reversal" with strong hydrochloric-acid eluant reported in ref. 12). Comparing homologous members of the two series for which information is available,

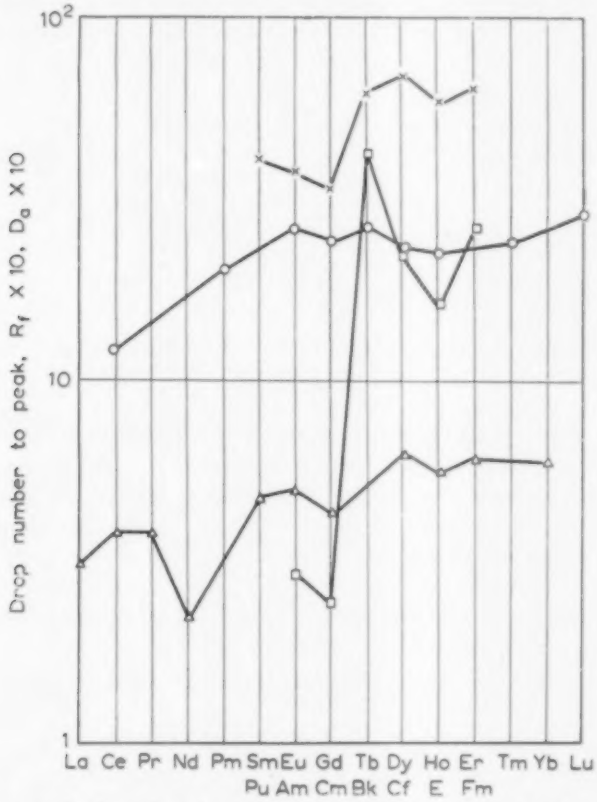

FIG. 6.—Complex formation of actinides and lanthanides as a function of atomic number.
× Actinide elution peak drop number from Dowex-1 with ammonium thiocyanate eluant.
○ Lanthanide elution peak drop number from Dowex-1 with ammonium thiocyanate eluant.
□ D_a for actinides from ref. 17.
△ R_f for lanthanides from ref. 18.

the same relative order is maintained, except for californium and dysprosium. In elution from Dowex-50, yttrium elutes near dysprosium and holmium, but here it elutes much sooner.

If the elution positions were determined solely from ionic radii considerations, then the order of elution from Dowex-1 should be just the order of increasing atomic number in both actinide and lanthanide series. Any particular actinide should elute near the lanthanide of similar ionic radius, and yttrium should elute near dysprosium and holmium. This expectation depends on the assumption that only "ionic" complexes with the same charge are formed. If covalent bonding is important in the

complex ion, the tendency toward complex-ion formation is not necessarily a function of the ionic radii. This might be the explanation of the fact that no simple elution sequence is observed within a series.

There are other indications that complex-ion formation in the actinides and lanthanides is not always solely dependent on the ionic radii. MAGNUSSON[17] has measured the distribution of some actinide ions between an aqueous phase (buffered with ammonium chloracetate) and a toluene phase 0·2 M in thenoyl trifluoro acetone. The results are given in terms of "*Da*," which is defined as the concentration ratio (toluene/aqueous, volume basis) of the ion studied. LEDERER[18] studied the paper chromatography of some lanthanide ions with acetyl acetone as complexing agent, giving the results in terms of an R_f defined as

$$\frac{\text{distance travelled by ion}}{\text{distance travelled by liquid front}}$$

The results of these investigations have been plotted in Fig. 6 also.

It can be seen from a point by point comparison of the curves that they are identical in shape, qualitatively, except for the californium elution position from Dowex-1 with ammonium thiocyanate and the difference between plutonium and americium compared to samarium and europium.

If certain simplifying assumptions are made, a quantitative estimate of the difference in free energy of formation of the complex ions may be made. Assume that only a single negatively charged species exists and sorbs on the resin. Because of their similar radii, the complex ions of americium and promethium should undergo sorption on the resin to the same extent. From experiment 3 in Table 4, the drop number to peak for promethium is 14 and for americium it is 121. Assume that this difference is entirely due to the difference in the formation constant of the complex ion. With these assumptions,

$$F^\circ(\text{Pm}) - F^\circ(\text{Am}) = RT \ln 121/14 = 1{\cdot}3 \text{ kcal} \qquad (11)$$

This is not a large difference in terms of chemical bonding energies. The change in free energy required to make an ion "reverse" its position with respect to another ion such as is observed in strong HCl with plutonium, americium, and curium is undoubtedly much less, probably of the order of 100 to 300 calories. Considering the energy involved, the tendency of the actinides to form stronger complexes than lanthanides could be due to the greater polarizability of the actinide ions.

The elutions from Dowex-50 failed to show a deviation from monatonic order which would have been observed if the relative elution positions were just the opposite of those from Dowex-1. Because of the similarity in ionic radii, americium usually elutes near promethium. From Dowex-50, americium eluted considerably sooner, as would be expected if americium complexes more strongly with SCN^- than does promethium.

The equations involved in the case of Dowex-50 are:

$$M^{+3} + 3NH_4R = MR_3 + 3NH_4^+ \qquad (12)$$

[17] L. B. MAGNUSSON and M. L. ANDERSON *J. Amer. Chem. Soc.* 6207 (1954).
[18] M. LEDERER *Compt. rend.* **236**, 1557 (1953).

(where "R" represents the immobile resin anion and "M^{+3}" the actinide or lanthanide ion)

and $$M^{+3} + xSCN^- = M(SCN)_x^{3-x}. \quad (13)$$

Now equation (13) is written identically with equation (5). However, there is one important difference. It was assumed that only negatively charged ions could be sorbed on the Dowex-1 resin, therefore the "x" in equation (5) must have a numerical value of 4 or greater. No such restriction exists for the value of "x" in equation (13). The equilibrium constant of equation (12) is large and this decreases the M^{+3} concentration in solution and, in turn, the concentration of the complex ion. If the formation of the complex ion occurs stepwise, the sorption of the $M(SCN)^{+2}$ and $M(SCN)_2^{+1}$ on the resin would tend to decrease further the complex-ion concentration in solution. On the other hand, when Dowex-1 resin is used, the formation of the complex ion in solution is favoured by its sorption on the resin. Therefore, elution from Dowex-1 probably gives a more direct measure of the relative strength of complex-ion formation, especially of the higher complexes, than does elution from Dowex-50. The implication, of course, is that equation (12) determines to a large extent the elution position of an ion. Under conditions more favourable for complex-ion formation (3 M NH_4SCN, 33°C) the order of elution is americium, lutetium, promethium from Dowex-50 4% cross-linked resin. But if Dowex-50 12% cross-linked resin is used under identical conditions, the order of elution becomes lutetium, americium, and promethium. This "reversal" of americium compared to promethium can only be attributed to the difference in sorption on the resin and clearly demonstrates the influence of equation (12) on the relative elution positions. It is not too surprising then that no "reversals" within the series occur on elution from Dowex-50 with ammonium thiocyanate and that the large differences in actinide-lanthanide behaviour observed in elution from Dowex-1 becomes less apparent.

Acknowledgements—The authors are grateful to Drs. B. B. CUNNINGHAM, S. G. THOMPSON, and B. G. HARVEY for discussions and suggestions which were of great assistance. The continued interest of Dr. GLENN T. SEABORG is gratefully acknowledged. Dr. J. O. RASMUSSEN donated the gadolinium alpha-emitting isotope. Mrs. ROBERTA GARRETT and Mrs. THERESE PIONTEKI assisted in the radiometric assays and counting. This work was performed under the auspices of the United States Atomic Energy Commission.

LETTER TO THE EDITORS

A preliminary spectrophotometric study of complex ions in fused salts*

(*Received* 29 *October* 1956)

It is the purpose of this communication to present some information recently obtained on absorption spectra of transition metal cations dissolved in fused salts and to point out the usefulness of the spectrophotometric technique for investigations of complex ions in such media.

The experiments were carried out with a Beckman Model DU spectrophotometer which was adapted for use at elevated temperatures. The usual cell compartment was replaced by a compartment of special design through which cooling water flows. Two 1 cm absorption cells can be accommodated in the cell holder which consists of a brass block with internal channels through which silicone oil is circulated from a constant temperature bath by means of a Tuthill direct displacement pump. The temperature of the bath can be held constant to $\pm 0{\cdot}5^{\circ}$ over long periods of time with a bimetallic thermoregulator. With this system the upper practical working temperature is 240°C. Salts used as solvents for the transition metal ions were first dried in an oven at 110°C, then melted in a beaker and further dehydrated by bubbling dry N_2 through the melt for 10–15 minutes. For each experiment, two 1 cm Corex absorption cells were filled with the melt and placed in the cell holder. To one of the cells, the appropriate anhydrous transition metal chloride was added to give an approximately 0·01 *M* solution. The other cell was used as a reference blank. During the taking of the spectra, the cell compartment was flushed with dry N_2 to prevent moisture from being absorbed by the sample. The work to be described was carried out in fused $LiNO_3$-KNO_3 eutectic (LiK nitrate, m.p. 132°C), but some preliminary observations have also been made in fused formates, thiocyanates, fluosulphonates, and chlorides. The following metal chlorides were dissolved in fused LiK nitrate: $MnCl_2$, $FeCl_2$, $CrCl_3$, UCl_4, $FeCl_3$, $CoCl_2$, $NiCl_2$, $CuCl_2$, UO_2Cl_2, $PrCl_3$, $NdCl_3$. Oxidation occurs with $MnCl_2$, $FeCl_2$, $CrCl_3$, and UCl_4. Absorption spectra were obtained of all the solutions except these four. The maxima of the absorption bands and their half-widths are listed in Table 1. For comparison with spectra in aqueous media, the maxima and half-widths in 1 M $HClO_4$ solutions are also given.

The spectra in fused LiK nitrate are displaced toward longer wavelengths and are somewhat broadened compared with aqueous solution spectra at room temperature. The extinction coefficients appear to be larger in the nitrate melt than in perchloric acid solutions. The factors are of the order 10–100 for Cu(II), Ni(II), Co(II) and 2–5 for U(VI), Pr(III), and Nd(III). The narrow bands so characteristic of aqueous solution spectra of the rare-earth ions are seen to be largely preserved in the fused salt solutions.

To study complex ion formation, anhydrous KCl was added to the fused nitrates and the spectra were re-examined after successive additions of KCl. Minimal changes were observed in the spectra of U(VI), Pr(III) and Nd(III) even at a chloride ion concentration of about 5 M, the solubility limit of KCl at these temperatures. Addition of KCl causes a shift toward longer wavelengths of the edges of the continuous absorption bands of Fe(III) and Cu(II), while in the case of Ni(II) the 425 mμ band is displaced toward longer wavelengths and develops a rather complex structure.

The effects of added KCl on the spectrum of a solution of $CoCl_2$ ($\sim$0·01 *M*) in fused LiK nitrate are shown in Fig. 1. Spectrum *A* contains no added chloride, while spectra *B*–*D* were obtained by adding successively larger amounts of KCl to the original solution. It is reasonable to assume that these spectral changes are associated with a change from hexacoordinated to tetracoordinated cobalt. This implies that the cobalt ion is surrounded by six nitrate groups in the pure nitrate melt.

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

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In the presence of chloride ion, however, the stepwise replacement of nitrate by chloride ions occurs resulting in the formation of the tetrahedral complex ion $CoCl_4^{=}$ which gives rise to absorption in the red region of the spectrum. This interpretation is analogous to that proposed by Katzin and Gebert to account for similar spectral changes occurring in aqueous and organic solutions of Co(II) on addition

TABLE 1.—ABSORPTION MAXIMA AND HALF-WIDTHS OF TRANSITION METAL IONS IN FUSED LiK NITRATE AND IN 1 M $HClO_4$ SOLUTIONS

Ion	LiK nitrate melt; 184°C		1 M $HClO_4$; 25°C	
	Absorption Maxima, mμ	Half-widths mμ	Absorption Maxima, mμ	Half-widths mμ
Fe(III)	No maximum. Complete absorption below 400 mμ	≈350	310	≈45
Cu(II)	850	75; 250	825	≈350
Ni(II)	425; 775	150	390; 710	60; 190
Co(II)	560	50	510	100
U(VI)	430	15; 15;	415	45
Pr(III)	447; 471; 485; 590	10; 25 7; 12;	444; 469; 483; 590	7, 7, 3, 13
Nd(III)	430; 513; 526; 585; 675; 739; 801; 871	7; 20; 15; 22; 17; 20	427; 512; 522; 575–578; 679; 742; 797–803; 868	2; 10; 7; 12; 17; 13; 13; 8

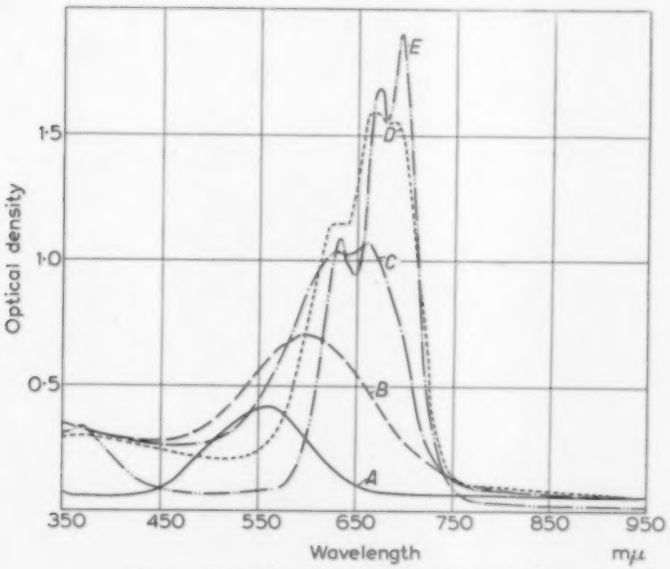

FIG. 1.—Absorption spectra of cobalt in fused salts.

Co(II) in fused $LiNO_3$-KNO_3 eutectic at 184°C
Co(II) in fused pyridine hydrochloride at 155°C

A———— No added chloride
B — — —
C — · —
D — — — —
E — ·· —
Increasing amount of chloride

of chloride ion.[1] Conclusions based on solution work have been reinforced by studies of reflection[2] and absorption[3] spectra of solid cobalt compounds like Cs_2CoCl_4 and $(HPy)_2CoCl_4$ (dipyridine cobalt tetrachloride) where the $CoCl_4^{=}$ group has been identified crystallographically.

In order to determine whether spectrum *D* represented essentially complete complexing of Co(II) by Cl^-, a spectrum was taken of a solution ($\approx$0·01 *M*) of $CoCl_2$ in fused pyridine hydrochloride[4] (m.p. 144·5°C). The spectrum of this solution (spectrum *E*) in which Co(II) finds itself in a pure Cl^- environment, closely resembles spectrum *D*. Moreover, there is a striking resemblance between spectra *D* and *E* and the main absorption band of solid Cs_2CoCl_4. (See Fig. 2 of reference 3.) There seems to be little doubt therefore that the pronounced absorption in the red region of the spectrum is due to the $CoCl_4^{=}$ ion in fused LiK nitrate with added chloride as well as in fused pyridine hydrochloride.

Recently, cryometric studies have been made of chlorocomplexes of Pb(II), Cd(II), and Zn(II) in fused $NaNO_3$.[5] These data were interpreted in terms of the stepwise formation of complexes $M^{+2} \rightarrow MCl_2 \rightarrow MCl_4^{=}$. The present work indicates that Co(II) and possibly Ni(II) behave in a similar fashion in fused LiK nitrate. In order to obtain quantitative information on the Co(II) and Ni(II) systems, a study is under way to determine the stability constants of the complexes and by making measurements over a range of temperatures to determine their heats and entropies of formation.

An application of this work to the chromatography of fused salts has been described recently.[6]

The help of J. B. GRUBER in the early stages of experimentation is gratefully acknowledged. The spectrophotometer compartment is based on a design of A. B. KRISCIUNAS. The author has had the pleasure of a number of fruitful discussions with L. I. KATZIN.

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[1] L. I. KATZIN and E. GEBERT *J. Amer. Chem. Soc.* **72,** 5464 (1950).
[2] L. I. KATZIN and E. GEBERT *ibid.* **75,** 2830 (1953).
[3] L. I. KATZIN *ibid.* **76,** 3089 (1954).
[4] L. F. AUDRIETH, A. LONG, and R. E. EDWARDS *ibid.* **58,** 428 (1936).
[5] E. R. VAN ARTSDALEN *J. Phys. Chem.* **60,** 172 (1956).
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EDITORIAL NOTE

High Energy Excitation Functions in the Heavy Region by W. W. MEINKE, G. C. WICK, and G. T. SEABORG, **3,** 69–92 (1956).

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J. Inorg. Nucl. Chem., 1957, Vol. 4, pp. 77 to 83. Pergamon Press Ltd., London

ISOTOPES OF EMANATION PRODUCED BY BOMBARDMENT OF GOLD WITH NITROGEN IONS*

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(*Received* 4 *October* 1956)

Abstract—Several emanation isotopes of very low neutron number have been prepared by bombardment of gold foil with 140-MeV nitrogen ions accelerated in the Berkeley 60-in. cyclotron. The alpha-decay properties of Em^{208}, Em^{207}, Em^{206}, and Em^{204} were measured. The alpha-decay to electron capture-decay ratios of Em^{206}, Em^{207}, Em^{208}, and of Po^{202} were determined.

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AN extensive study of the properties of the light isotopes of emanation, francium, and radium has been published by MOMYER and HYDE.[1] This study showed the pronounced influence of the 126-neutron shell on the properties of the isotopes of these elements. In the case of the element emanation, considerable information was found by the above authors on the nuclear properties of Em^{212}, Em^{211}, Em^{210}, Em^{209}, and Em^{208}. These isotopes were prepared by high-energy spallation of thorium targets with 340-MeV protons.

It seemed desirable to extend the studies of MOMYER and HYDE to even lower mass numbers. It was not very feasible to do this by the examination of the emanation fraction from thorium targets because of the interference from the radiations of the isotopes listed above. This difficulty can be neatly circumvented by another preparative approach; namely, the bombardment of gold targets with nitrogen ions. Using nitrogen ions from the Berkeley 60-in. cyclotron with energies up to 140 MeV, it has been possible to carry out reactions of the type $Au^{197}(N^{14}, xn)Em$. The number of neutrons released, x, turned out to be three or more in our experiments, resulting in the production of emanation isotopes of mass number 208 or less. It was possible to measure the principal decay characteristics of Em^{208}, Em^{207}, Em^{206}, and Em^{204}. The detailed description of these isotopes and of the astatine and polonium daughter activities is given in the experimental section below. A preliminary summary of our work was included in the publication of MOMYER and HYDE cited above. A similar study was carried out simultaneously by BURCHAM.[2] Our results are in agreement with his except for a somewhat different value for the α/EC branching of Em^{207}.

EXPERIMENTAL

The emanation isotopes were produced by bombarding gold with nitrogen ions which were accelerated in the 60-in. cyclotron of the Crocker Radiation Laboratory. Only the +6 species of nitrogen ions are accelerated to energies high enough to penetrate the potential barrier of gold and cause a nuclear reaction. The mechanism of formation and acceleration of the +6 ions of nitrogen

* This work performed under the auspices of the United States Atomic Energy Commission.
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[1] F. F. MOMYER and E. K. HYDE *J. Inorg. Nucl. Chem.* **1**, 274 (1955).
[2] W. E. BURCHAM *Proc. Phys. Soc.* **A67**, 555 (1954).

has been discussed by CHACKETT, FREMLIN, and WALKER,[3] and by ROSSI and co-workers.[4] The beam achieved with the 60-in. cyclotron consists of +6 nitrogen ions with a continuous energy distribution up to approximately 140 MeV. The beam intensity above 100-MeV energy is greater than 0·1 μA. The $N(+2)$ beam intensity is about 50 μA and adds greatly to target heating, but is too low in energy to surmount the potential barrier. The gold target is mounted so that it intercepts the beam at the outer edge of the cyclotron dees, and can be cooled by a flow of water behind the foil.

5-mil gold foils were used in these experiments, and the whole assembly was designed so that the foil could be removed very quickly in order to facilitate the study of isotopes with short half-lives.

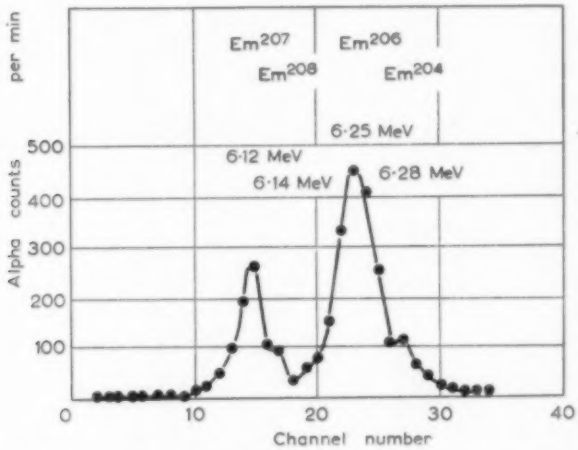


FIG. 1.—Alpha spectrum of Em^{208}, Em^{207}, Em^{206}, and Em^{204}. A 1-min run taken 12 min after bombardment.

The extraction of the emanation was accomplished by amalgamating the gold foil with mercury in a vacuum system. The amalgam was heated with an induction heater to speed up the dissolution of the gold and the heating also caused agitation of the sample. The gases evolved were passed through a U-tube which was maintained at the temperature of dry ice-acetone mixture and condensed in another U-tube cooled by liquid nitrogen. Samples for counting were prepared by the glow-discharge procedure as outlined by MOMYER and HYDE.[1] A period of 15 to 20 min elapsed from the end of bombardment until the foil-mounted, purified emanation fraction was ready for alpha counting in our ionization chamber-pulse height analyser. The differential pulse height analyser has forty-eight electronic channels to analyse the pulses developed from the ionization chamber. This instrument is a modification of an original design by GHIORSO *et al.*[5]

The alpha-particle energy spectrum of the emanation sample as observed during a 1-min run taken 21 min after the end of bombardment is shown in Fig. 1. Alpha peaks were observed at 6·12 and 6·25 MeV, with small shoulders on these peaks at 6·14 and 6·28 MeV. The alpha spectrum of this sample was retaken at short intervals until the alpha peaks had decayed in order to establish half-lives for each.

The measured half-lives and the mass-number assignment of the activities are tabulated in Table 1. The mass assignments were determined by genetic relationships to daughter astatine and polonium isotopes, as will be discussed. The alpha to electron-capture decay ratio was determined for several isotopes, and these values are also recorded in Table 1.

[3] K. F. CHACKETT, J. H. FREMLIN, and D. WALKER *Proc. Phys. Soc.* **A66**, 495 (1954).
[4] G. B. ROSSI, W. B. JONES, J. M. HOLLANDER, and J. G. HAMILTON *Phys. Rev.* **93**, 256 (1954).
[5] A. GHIORSO, A. H. JAFFEY, N. P. ROBINSON, and B. WEISSBOURD *The Transuranium Elements* National Nuclear Energy Series, Plutonium Project Record; Research Papers, Vol. 14B, Paper 16·8, McGraw-Hill Book Company, Inc., New York, (1949).

TABLE 1.—PROPERTIES OF OBSERVED ISOTOPES

Isotope	Half-life (min)	Alpha-particle energy (MeV)	Electron-capture branching	Alpha branching
Em^{208}	21 ± 3	$6{\cdot}14 \pm 0{\cdot}05$	80%	20%
Em^{207}	10 ± 2	$6{\cdot}12 \pm 0{\cdot}05$	96%	4%
Em^{206}	$6{\cdot}2 \pm 0{\cdot}5$	$6{\cdot}25 \pm 0{\cdot}05$	35%	65%
Em^{204}	3 ± 1	$6{\cdot}28 \pm 0{\cdot}05$	—	—
At^{207}	107 ± 5	$5{\cdot}75 \pm 0{\cdot}05$	~90%	~10%
Po^{202}	51 ± 3	$5{\cdot}57 \pm 0{\cdot}05$	98%	2%

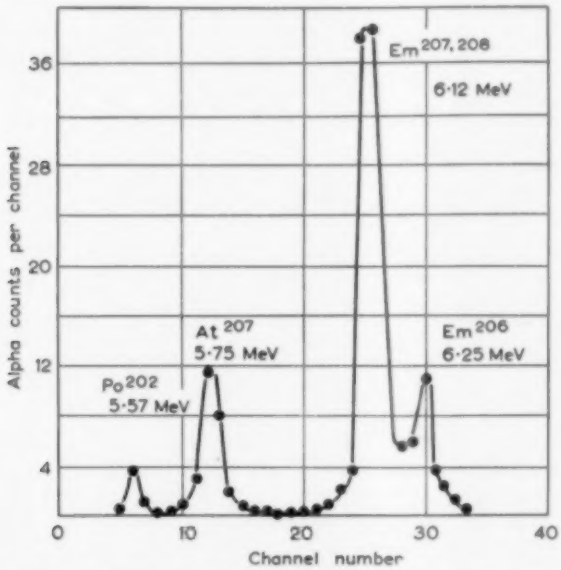


FIG. 2.—Alpha spectrum of At^{207} and Po^{202} daughter activities growing into sample. A 10-min run taken 40 min after end of bombardment.

The alpha-emitting astatine and polonium daughter activities of the emanation isotopes can be observed to grow into the samples. An alpha spectrum taken for 10 min, starting 40 min after the end of the bombardment is shown in Fig. 2. The alpha group from Po^{202} and the alpha group from At^{207} daughters can easily be observed in addition to residual peaks in the unresolved Em^{207}–Em^{208}, and Em^{206}–Em^{204} peaks. The half-life and alpha-particle energy for Po^{202} and At^{207} are also included in Table 1. Alpha groups from the decay of Po^{208} and Po^{206} were also observed 24 hours later by taking a 4-hour count.

DETERMINATION OF MASS ASSIGNMENTS OF ACTIVITIES

A. *Emanation*-208

The assignment of the 21 ± 3 min half-life and the $6{\cdot}14 \pm 0{\cdot}05$ MeV alpha group to Em^{208} was made by comparing these values with previously reported values for Em^{208}. MOMYER and HYDE observed a 23-min half-life in an emanation sample prepared by the high-energy proton spallation of thorium metal.[1] MOMYER, ASARO,

and HYDE measured the alpha-particle energy to be 6·138 ± 0·005 MeV on a magnetic alpha-particle spectrograph.[6] They assigned the activity to Em^{208} by observing the growth of Po^{204} and Po^{208}. The alpha-particle energy and the half-life measured in our experiment agree within experimental error with these previously published values. This agreement, in addition to the fact that Po^{208} was observed as a decay product in our samples, makes certain the assignment of the 6·14-MeV peak to Em^{208}.

B. *Emanation*-207

The alpha group at 6·12 MeV was observed to decay with a 10-min half-life. This activity was assigned to Em^{207} by observing the growth and decay of the alpha activity of At^{207}. The genetic relationships involved in this case are the following:

$$\underset{10\text{ min.}}{Em^{207}} \xrightarrow{EC\,(96\%)} \underset{105\text{ min.}}{At^{207}} \xrightarrow{EC\,(90\%)} \underset{5\text{·}7\text{ hour}}{Po^{207}} \xrightarrow{EC(90+\%)}$$

$$\alpha\,(4\%) \downarrow \qquad \alpha\,(10\%) \downarrow$$

$$Po^{203} \qquad Bi^{203}$$

From the laws of radioactive decay the number of alpha disintegrations of At^{207} present at any time in an initially pure sample of Em^{207} is given by the expression

$$\left(\frac{dB}{dt}\right)_{\alpha} = \frac{-A_0\lambda_A\lambda_B f_A^{EC} f_B^{\alpha}}{\lambda_B - \lambda_A}\left(e^{-\lambda A t} - e^{-\lambda B t}\right) \tag{1}$$

where A_0 is the initial number of atoms of Em^{207}, B is the number of atoms of At^{207}, λ_A and λ_B are the total disintegration-rate constants, f_A^{EC} is the fraction of Em^{207} atoms disintegrating by electron capture, f_B^{α} is the fraction of At^{207} atoms disintegrating by alpha emission, and t is the time.

In Fig. 3 the experimental points showing the growth and decay of 5·75 MeV alpha particles of At^{207} are compared with theoretical curves based on half-lives of 7, 10, and 13 min for Em^{207}; the theoretical curves are normalized to the experimental points at the maximum because f_A^{EC} was not known. The 10-min line gives the best fit.

The location of the time, $t_{max.}$ corresponding to the maximum activity of At^{207} is given by the expression:

$$t_{max} = \frac{1}{\lambda_A - \lambda_B}\ln\frac{\lambda_A}{\lambda_B} \tag{2}$$

This expression is independent of the branching ratios in either isotope. Using the measured half-life of 10 min for Em^{207} and 107 min[7] for At^{207}, the time at maximum activity is calculated to be 40 min by equation (2). This corresponds to the experimental value of 39 ± 4 min taken from the experimental curve in Fig. 3. It is concluded that the 10-min activity emitting alpha particles of 6·12 MeV is Em^{207}.

The branching ratio for Em^{207} can be calculated from the alpha disintegration rate of Em^{207} and the alpha disintegration rate of At^{207}. At^{207} is the product of the electron-capture decay of Em^{207}, and its alpha activity gives a measure of the amount

[6] F. F. MOMYER, F. ASARO, and E. K. HYDE *J. Inorg. Nucl. Chem.* **1**, 267 (1955).
[7] G. BARTON, A. GHIORSO, and I. PERLMAN *Phys. Rev.* **82**, 13 (1951).

of electron capture which Em^{207} undergoes. This alpha branching of At^{207} has previously been measured to be approximately 10%.[7] Taking the At^{207} alpha activity at any time, the number of atoms of Em^{207} that are required to give rise to this amount of At^{207} activity can be easily calculated. By comparing this number with the number

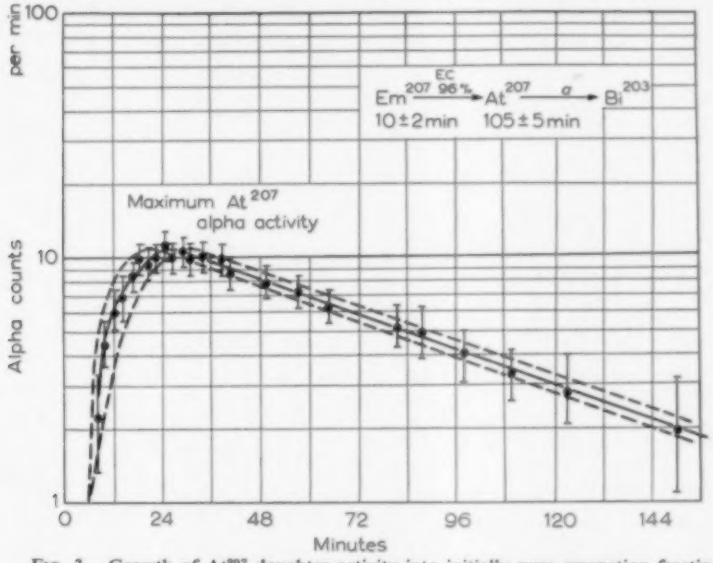
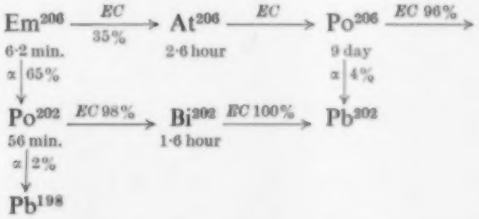


FIG. 3.—Growth of At^{207} daughter activity into initially pure emanation fraction.
— — — = Growth curves for a 7- and 13-min half-life parent

of Em^{207} atoms required to give the observed Em^{207} alpha disintegration rate, the amount of alpha and electron-capture decay of Em^{207} can be determined. The average of two experiments gave a value of 4% alpha and 96% electron-capture decay. Since the 10% alpha-branching of At^{207} upon which this calculation is based is known only approximately, the Em^{207} alpha branching is also only an approximate value.

C. *Emanation*-206

The assignment of the 6·2-min half-life and the 6·25 ± 0·05-MeV alpha group to Em^{206} was achieved by observing the growth of the alpha daughter, Po^{202}. Po^{202} has been assigned a 52-min half-life by KARRAKER and TEMPLETON[8] and an energy of 5·575 by ROSENBLUM and TYRÉN.[9] The genetic relationships in this case are the following:



[8] D. G. KARRAKER and D. H. TEMPLETON *Phys. Rev.* **81**, 510 (1951).
[9] S. ROSENBLUM and H. TYRÉN *Compt. rend.* **239**, 1205 (1954).

The growth of the Po^{202} was observed by measuring the counting rate of its 5·57-MeV alpha group. The maximum amount of Po^{202} alpha activity was found to occur at 20 min after purification of the Em^{206}. This value agrees with the calculated t_{max} of 19·5 min for Po^{202} activity found, using 6 mm for the Em^{206} half-life and an equation analogous to equation (2). This excellent agreement between the calculated and experimental t_{max} and the fact that parent half-lives of 4 min or 10 min gave t_{max} values

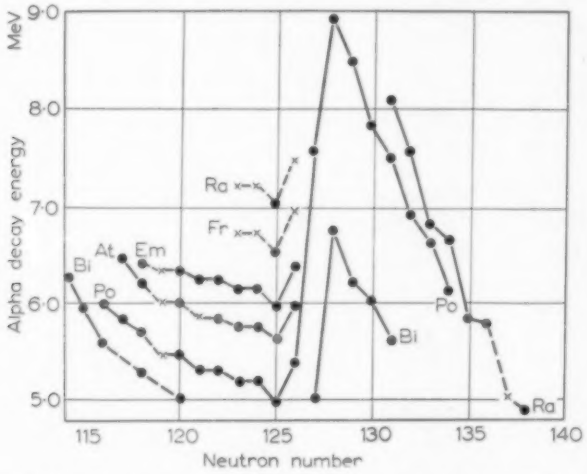


FIG. 4.—Alpha disintegration energy versus mass number plots. (Alpha disintegration energy includes alpha-particle energy plus nuclear-recoil energy).
● measured energy.
× estimated energy.

far outside the experimental error of the determination, makes this mass assignment reasonably certain. The growth of At^{206} could not be observed in order to further check the mass assignment because of the absence of a measurable alpha branching of At^{206}.

The ratio of alpha-emission to electron-capture branching for Em^{206} was determined by comparing the alpha disintegration rate of Em^{206} with the alpha disintegration rate of Po^{206}. Po^{206} is related to Em^{206} through At^{206}, the immediate product of the electron-capture branching of Em^{206}. At^{206} decays 100% by orbital electron capture to Po^{206}. The Po^{206} alpha activity when corrected for its 96% electron-capture decay is a measure of the amount of electron capture of Em^{206}. Hence, by comparing the alpha disintegration rate of Po^{206} with the alpha activity of the Em^{206} originally in the sample, one can calculate the alpha branching of Em^{206}. This comparison was made in several experiments and yielded the values of 65% for the alpha branching and 35% for the electron-capture branching decay.

From this same data the alpha branching of Po^{202} can be determined. The Po^{202} is only produced as the daughter of the alpha decay of Em^{206}. From the alpha disintegration rate of Em^{206}, the number of atoms of Po^{202} at any time can be calculated. The observed alpha disintegration rate of Po^{202} gives the number of these atoms that are undergoing alpha decay. This gives a direct measurement of the Po^{202} alpha branching, which was determined to be 2%.

D. *Emanation*-204

The 3-min 6·28-MeV activity could be either Em^{204} or Em^{205}, and has been assigned to Em^{204} on the basis of alpha systematics, since it was impossible to assign it directly on the basis of identification of product activities. The alpha-branching ratio of Po^{200} or of the At^{204}–Po^{204} pair which would arise from the alpha decay and the electron-capture decay, respectively, of Em^{204} are unknown but very probably are so low that the alpha groups would not be observable in our experiments. Similarly, the Po^{201} daughter of an hypothetical Em^{205} alpha decay would not be observable. Perhaps the alpha particles of At^{205}, the electron-capture decay daughter of Em^{205}, should be observable, but the alpha branching of At^{205} is not known.

The choice of mass number 204 was made for the following reasons. Since the alpha branching of Em^{209} is ~20% and that of Em^{207} 4%, one might expect that the alpha branching of Em^{205} would be so low that it would be unobservable in our experiments. On the other hand, the alpha branching of the even isotopes of emanation remain high throughout the mass region. Hence, one might expect Em^{204} to decay prominently by alpha emission.

Additional evidence for the assignment comes from an inspection of Fig. 4, which shows the alpha disintegration energy versus mass number. The placement of the 3-min 6·28-MeV (6·4-MeV total disintegration energy) activity as ${}_{86}Em^{204}_{118}$ fits in well with the regularities noticed throughout this mass region, particularly the regularity that an odd-mass isotope has nearly the same alpha disintegration energy as the next higher even-mass isotope. Placement of this activity as ${}_{86}Em^{205}_{119}$ would definitely be out of line with the regularities in the 119–124-neutron region for the isotopes of emanation, astatine, and polonium.

Acknowledgements—The authors wish to express their appreciation to A. Ghiorso, W. Jones, the late G. B. Rossi, and the crew of the 60-in. cyclotron for their co-operation in making these nitrogen-ion bombardments possible.

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THE CRYSTAL STRUCTURE OF GALLIUM DICHLORIDE

G. GARTON* AND H. M. POWELL†

(*Received* 27 *October* 1956)

Abstract—The crystal structure of gallium dichloride consists of tetrahedral $[GaCl_4]^-$ ions and Ga^+ ions. The orthorhombic unit cell ($a = 7{\cdot}24$ Å, $b = 9{\cdot}72$ Å, $c = 9{\cdot}50$ Å) contains $4Ga_2Cl_4$, and the space group is *Pnna*. Each Ga^+ ion has eight nearest neighbours, all Cl atoms from surrounding $GaCl_4$ groups, disposed at the corners of a dodecahedron similar to that found in the molybdenum octocyanide ion, $[Mo(CN)_8]^{4-}$.

THE empirical formula of gallium dichloride, $GaCl_2$, suggests that in it gallium is divalent, whereas the common valencies of group IIIB elements are 1 and 3. However, the empirical formula for a crystalline substance is often misleading, and for the analogous indium and thallium dihalides it has been suggested that the composition arises from equal proportions of monovalent and trivalent metal atoms. Objection has been made to the formulation $Ga(I)^+[Ga(III)X_4]^-$ for the gallium dihalides on the grounds that monovalent gallium was not well established,[1] the evidence until recently being limited to a few poorly characterized compounds of gallium with the elements of group VIB. Recently, gallium monochloride,[2] monobromide,[3] and monoiodide[4] have all been prepared, and this objection no longer holds. An alternative constitution for gallium dihalides[5] involving a Ga-Ga bond has also been proposed. Such bonds were found in the crystal structure of metallic gallium and have been reported to be present in crystalline GaS[6] and GaSe.[7] Either of these formulations is consistent with the diamagnetism of gallium dichloride.[5] WOODWARD, GARTON, and ROBERTS[8] have deduced from the Raman spectrum that $GaCl_4^-$ ions are present in fused gallium dichloride. CORBETT and MCMULLAN[9] recently stated that gallium dichloride has the structure $Ga(I)^+[Ga(III)Cl_4]^-$, but do not give the method of investigation on which this conclusion is based. The present X-ray investigation establishes the constitution in the crystalline state.

EXPERIMENTAL

5 g of gallium (Johnson, Matthey & Co., 99·9% pure) was converted into gallium trichloride by gently heating it in a stream of pure, dry chlorine. The trichloride was redistilled *in vacuo* into a reaction bulb containing a further 2·5 g gallium. The bulb was sealed off and maintained at 180°C for 24 hours, with occasional shaking. The product was vacuum-distilled at about 200°C into another bulb and sealed off from the reaction vessel. This bulb, which had a long neck, was then kept at

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[1] N. V. SIDGWICK *Chemical Elements and their Compounds*, p. 477.
[2] E. GASTINGER *Angew. Chem.* **67**, 103 (1955).
[3] F. M. BREWER, G. GARTON, and S. M. ALI To be published.
[4] J. D. CORBETT and R. K. MCMULLAN *J. Amer. Chem. Soc.* **77**, 4217 (1955).
[5] W. KLEMM and W. TILK *Z. anorg. Chem.* **207**, 161 (1932).
[6] H. HAHN and G. FRANK *Z. anorg. Chem.* **278**, 333 (1955).
[7] K. SCHUBERT and E. DORRE *Naturwiss.* **40**, 604 (1953).
[8] L. A. WOODWARD, G. GARTON, and H. ROBERTS *J. Chem. Soc.* 3723 (1956).
[9] J. D. CORBETT and R. K. MCMULLAN *J. Amer. Chem. Soc.* **78**, 2906 (1956).

180°C in an electric oven with the top few centimetres of the neck projecting and cooled by an air-blast. Any gallium trichloride was thus distilled into the cooler top section of the neck, where, after 24 hours, it was sealed off. The dichloride was run into the remaining section of the neck, which was sealed off and later broken under a layer of moisture-free medicinal paraffin. This oil, which does not react with or dissolve the dichloride, protected it from atmospheric attack. On heating the oil to 175°C, the dichloride fused and ran out of the tube to the bottom of the vessel. The fused gallium dichloride was cooled very slowly until crystals began to form. Since it had a strong tendency to supercool and solidify suddenly, it had to be remelted and recooled several times until only a few crystals remained at the melting-point. Slow cooling then produced a crop of needle-shaped crystals growing in clusters from the seeds. Single crystals about 0·2 mm diameter were selected and while still protected by the paraffin were manipulated into fine Lindemann-glass capillary tubes, which were then sealed. Needle-shaped crystals aligned themselves roughly with the axis of the tube, so that oscillation about the needle axis was easily achieved. Fragments broken from needles were adjusted inside capillaries with a fine glass fibre until the needle axis was roughly perpendicular to the tube length. Some had b nearly parallel to the tube length and were used for oscillation about that axis. Weissenberg photographs were taken with nickel-filtered copper radiation on a "Unicam" instrument. Layers up to the third about the a axis and the fourth about the b axis were recorded by the equi-inclination method. Relative intensities were estimated visually from multiple films.

STRUCTURE DETERMINATION

The orthorhombic unit cell has $a = 7{\cdot}24$ Å, $b = 9{\cdot}72$ Å, $c = 9{\cdot}50$ Å, with the probable limits of error $\pm 0{\cdot}02$ Å. The absent spectra $hk0$ when h is odd, $h0l$ when $h + l$ is odd, and $0kl$ when $k + l$ is odd, indicate the space group *Pnna*. In this, the general position is eightfold, and there are special positions of fourfold multiplicity. Pyknometric determination of the density of the crystalline dichloride gave the value 2·74 g/c.c., corresponding to a unit-cell content of eight gallium and sixteen chlorine atoms.

Patterson projections were made perpendicular to [100] and [010]. Trial was first made of the possibility that the gallium atoms occupied a general position. Co-ordinates were selected so that the set of Ga-Ga vectors was compatible with some of the stronger peaks of the [100] projection. An F_{0kl} synthesis was made by the use of structure factor signs based on the gallium contributions only. Small peaks appeared on the assumed gallium positions, but larger ones were found elsewhere. It was not possible to develop the structure further, and it was concluded that the gallium atoms must occupy two sets of fourfold positions.

All possible ways of selecting two separate sets of four atoms were considered for compatibility with the Patterson projections. It was concluded that 4Ga lie at $\frac{1}{4},0,z$ (position (*c*) as listed in the International Tables for X-ray Crystallography), and 4Ga at $x,\frac{1}{4},\frac{1}{4}$ in position (*d*). The signs of F_{0kl} were determined on the basis of Ga contributions only, and a Fourier electron density synthesis made. The projection showed the Ga atoms where they had been introduced, and small peaks revealed the positions of the Cl atoms in two sets of eightfold general positions (*e*). The signs of F_{0kl} were redetermined from the contributions of all atoms in the unit cell, and the recalculated Fourier synthesis showed all atoms close to the assumed positions and well resolved. The projection suggested that each gallium atom of one fourfold set (*c*) was surrounded by 4Cl atoms in the form of a regular tetrahedron. On this assumption, and with the help of the Patterson projection perpendicular to [010], the x co-ordinates of all the atoms were deduced and the signs of F_{h0l} calculated accordingly. An F_{h0l} synthesis confirmed the postulated structure. In both projections all the atoms were clearly resolved. Presumably, owing to the ionic character

TABLE 1.—OBSERVED AND CALCULATED STRUCTURE FACTORS

h k l	F_{obs}	F_{calc}	*h k l*	F_{obs}	F_{calc}
0 0 2	150	−170	0 10 2	39	32
0 0 4	81	86	0 10 4	34	−32
0 0 8	81	−85	0 11 1	42	47
0 1 1	50	54	0 11 3	38	−38
0 1 3	21	16	0 11 5	34	38
0 2 0	39	28	0 12 0	31	46
0 2 2	71	−67	1 0 1	41	−41
0 2 4	95	−102	1 0 3	110	−120
0 2 6	137	161	1 0 5	56	44
0 2 8	82	−101	1 0 7	158	−134
0 2 10	54	77	1 0 9	83	68
0 3 1	79	−73	2 0 0	93	−110
0 3 3	74	−73	2 0 4	47	−50
0 3 5	47	30	2 0 6	54	43
0 3 7	42	33	2 0 10	41	38
0 3 11	31	32	3 0 1	42	42
0 4 0	140	173	3 0 5	39	−47
0 4 2	155	−170	3 0 7	60	46
0 4 4	56	53	3 0 9	47	−32
0 4 6	26	12	4 0 0	94	82
0 5 1	73	73	4 0 2	87	−105
0 5 3	46	−36	4 0 4	29	−27
0 5 5	39	39	4 0 6	84	91
0 5 7	42	−28	4 0 8	77	−51
0 5 9	27	−40	4 0 10	52	50
0 6 0	71	43	5 0 1	89	−83
0 6 2	69	72	5 0 3	74	92
0 6 4	47	−48	5 0 5	45	44
0 6 6	73	52	5 0 9	16	16
0 6 8	81	−84	6 0 0	63	79
0 7 1	54	43	6 0 4	44	45
0 7 3	70	−65	6 0 6	48	−49
0 7 5	73	54	7 0 1	58	48
0 8 0	26	25	7 0 3	55	−62
0 8 2	91	−79	8 0 0	29	23
0 8 4	42	33	8 0 2	33	−15
0 9 3	84	−83	8 0 6	46	57
0 9 5	56	58	9 0 1	46	−55

of the structure, the F values do not fall off very rapidly with increasing sin θ, and the most likely errors are those due to termination of series. Accordingly, refinement of the structure was carried out by means of the difference syntheses of $(F_{obs} - F_{calc})$ for the zones 0*kl* and *h*0*l*. Consequent minor changes in the parameters from the values indicated by the peak positions of the F synthesis gave an improvement in the disagreement factor:

$$R = \Sigma \left| F_{obs} - F_{calc} \right| / \Sigma \left| F_{obs} \right| .$$

For all observed 0*kl* and *h*0*l* reflections up to sin $\theta = 0{\cdot}9$, R was reduced to 0·146.

When all F's too weak for observation are included with half the threshold value, $R = 0{\cdot}171$. Table 1 gives the observed and calculated structure factors. In the observed F's no allowance is made for absorption. The observed values have been scaled by comparison with the final calculated values. For nine of the ten most intense reflections, F_{calc} is greater than F_{obs}; this is probably an extinction effect. F's were calculated with atomic scattering factors taken from the International Tables for X-ray Crystallography, and a temperature factor with $B = 2{\cdot}0$ Å^2 was determined by WILSON's method.[10] All $h0l$ and $0kl$ reflections for which $\sin\theta < 0{\cdot}9$ were considered. Those which were not observed are omitted from the Table. For all except two of these, the calculated F was equal to or less than that corresponding to the threshold of observation. *303* ($F_{obs} < 20$, $F_{calc} = 36$) and *202* ($F_{obs} < 20$, $F_{calc} = 27$) are the only exceptions. The final Fourier projections of electron density perpendicular to [100] and [010] are shown in Figs. 1 and 2, and the atomic co-ordinates are given in Table 2.

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TABLE 2.—ATOMIC CO-ORDINATES

Atom	Position		x	y	z
Ga(I)	(*d*)	fourfold	0·681	¼	¼
Ga(III)	(*c*)	fourfold	¼	0	0·183
$Cl_{(1)}$	(*e*)	eightfold	0·339	0·174	0·054
$Cl_{(2)}$	(*e*)	eightfold	0·010	0·048	0·315

DESCRIPTION OF THE STRUCTURE

The structure is composed of $GaCl_4^-$ tetrahedra and Ga^+ ions. The Ga-Cl bond in the tetrahedron has a length 2·19 Å, which may be compared with the length of 2·22 Å for the Ga-Cl bonds in the vapour of Ga_2Cl_6, as determined by electron diffraction.[11] The distance from Ga(III) to the outer edge of its attached Cl atoms is about 4 Å, so that the complex anion is rather large in relation to the cation radius. In the structure there are accordingly many contacts between Cl atoms of different complex ions, and the cation and complex anion are not related to each other by the structural plan of any simple ionic AX compound. Their disposition also differs from those arrangements found amongst a number of compounds of formally similar constitution, such as $KClO_4$, $CaSO_4$, $CaWO_4$, $AlAsO_4$, $ZrSiO_4$.

Looking along the b axis an observer sees a kinked row of Ga(III) atoms ringed by Cl atoms. "Chains" of this kind are centred on ¼,0,¼ and ¾,0,¾. The Ga^+ ions lie between these chains in similar kinked rows centred on ¼,0,¾ and ¾,0,¼. Each Ga^+ ion is surrounded by eight Cl atoms, from six different tetrahedra, at the corners of an irregular dodecahedron. Four Cl atoms are at 3·18 Å from the Ga^+ ion and four at 3·27 Å. The shortest Cl–Cl distances in the co-ordination polyhedron are 3·8 Å. This polyhedron, illustrated in Fig. 3, is a slightly distorted form of the zirconium co-ordination found in zircon and the similar co-ordination in the complex molybdenum octocyanide ion $[Mo(CN)_8]^{4-}$.

[10] A. J. C. WILSON *Nature* **150**, 152 (1942).
[11] D. P. STEVENSON and V. SCHOMAKER *J. Amer. Chem. Soc.* **64**, 2514 (1942).

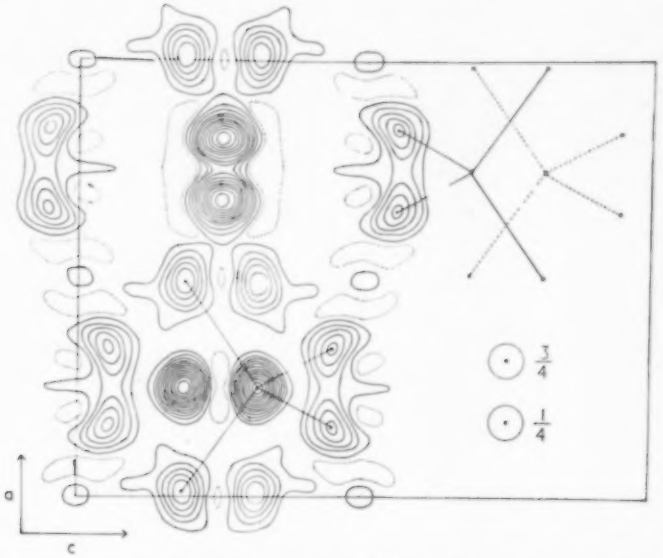

FIG. 1.—Fourier synthesis of electron density projected perpendicular to [010]. Contours are drawn over approximately half the unit cell at intervals of 5 e/Å². Zero contour dotted. In the other part of the unit cell, $GaCl_4^-$ tetrahedra are indicated by full and broken lines with the central Ga(III) atoms at $y = 0$ and $y = \frac{1}{2}$ respectively. Circles show the positions of $Ga(I)^+$ ions at $y = \frac{1}{4}$ and $y = \frac{3}{4}$. The projection has a centre of symmetry.

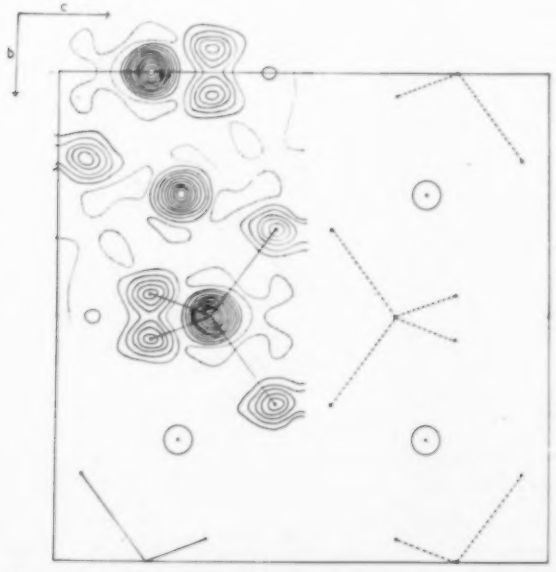

FIG. 2.—Fourier synthesis of electron density projected perpendicular to [100]. Contours are drawn over approximately a quarter of the unit cell at intervals of 5 e/Å². Zero contour dotted. In the other part of the unit cell, $GaCl_4^-$ tetrahedra are indicated by full and broken lines with the central Ga(III) atoms at $x = \frac{1}{4}$ and $x = \frac{3}{4}$ respectively. Circles show the positions of $Ga(I)^+$ ions at $0{\cdot}181,\frac{1}{4},\frac{1}{4}$; $0{\cdot}319,\frac{3}{4},\frac{3}{4}$; $0{\cdot}819,\frac{3}{4},\frac{1}{4}$. The projection has a centre of symmetry.

In view of the state of co-ordination, the effective radius of a Cl atom of the $GaCl_4$ complex for contact with the cation is unlikely to be greater than 1·81 Å, the crystal radius of Cl^-. The effective radius of the Ga^+ ion calculated from the interatomic distance Ga^+–Cl thus has a minimum value of 1·37 Å, which, on correction for co-ordination number, would require a crystal radius 1·33 Å for Ga^+. This appears

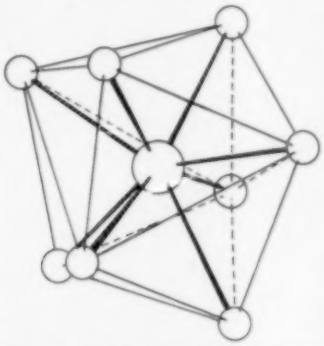

FIG. 3.—Co-ordination polyhedron of the gallous ion. *a* axis vertical.

to be large. Tl^+ has a radius of 1·44 Å, and a decrease of at least 0·3 Å for its analogue two periods earlier in the Periodic Table might be expected from the behaviour of neighbouring groups. The radius of the intermediate In^+ would be of use in deciding on a probable radius for Ga^+, but no reliable value is available. The figure 1·84 Å for the "van der Waals radius (ionic)" has been deduced from the structure of InBr,[12] but the bonding in this crystal is of a complex kind and the structure is not suitable for estimating ionic radii. The Ga^+–Cl distance now found is probably misleadingly large, owing to the contacts of anion with anion; if so, the apparent crystal radius 1·33 Å of the Ga^+ ion is also deceptively large.

Acknowledgement—One of us (G. G.) wishes to thank Imperial Chemical Industries Ltd. for a Research Fellowship.

[12] N. C. STEPHENSON and D. P. MILLER *Aust. J. Sci. Res.* A3, 581 (1950).

J. Inorg. Nucl. Chem., 1957, Vol. 4, pp. 90 to 92. Pergamon Press Ltd., London

INFRA-RED SPECTRA OF INORGANIC SOLIDS—I

PEROXIDES, PEROXIDE HYDRATES, AND SUPEROXIDES

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Abstract—A number of peroxide, peroxide hydrate, and superoxide samples were scanned in the rock salt region of the infra-red. For this scan, a special modification of the KBr disc technique was developed. The spectra show only carbonate and water to be the major impurities except for the hydrate samples where water is already combined. An indication of any structural detail for these hydrate samples was not observed.

THE use of infra-red absorption spectra for identification purposes in inorganic chemistry has become more practicable in recent years with the development of the KBr disc method for solids.[1, 2] Even so, the actual number of inorganic materials which have been examined is small. In the excellent summary of MILLER and WILKINS[3] there are no patterns shown for any inorganic peroxides, peroxide hydrates, or superoxides, although a few organic peroxides and hydroperoxides have been studied.[4, 5, 6] In connection with other work concerning the analysis and characterization of inorganic peroxides, peroxide hydrates, and superoxides, we have obtained the infra-red spectra of Li_2O_2, $Li_2O_2 \cdot 8H_2O$, Na_2O_2, $Na_2O_2 \cdot 8H_2O$, $Na_2O_2 \cdot 8D_2O$, NaO_2, KO_2, CaO_2, $CaO_2 \cdot 8H_2O$, SrO_2, and BaO_2. This was done in order to search for a possible existence of an O_3^{-1} ion as well as to investigate the structure of peroxide hydrates.

EXPERIMENTAL

In order to prevent water and carbon dioxide from coming into contact with the sample during sample preparation for the infra-red examination, all work was carried out in a dry box. This excludes the hydrate samples which were prepared in a cold room. A special technique for sample preparation resulted in a modification of the KBr disc procedure. For this modification, about 2 mg of sample and 200 mg of KBr powder were ground and mixed together by hand in a mortar. Following the mixing, a smooth layer of KBr powder was placed at the bottom of the mold. The sample mixture was then transferred from the mortar and was smoothed out on top of the KBr layer. Finally, another layer of KBr powder was placed on top and also made smooth. The net result was a sandwich of the sample mixture between two KBr layers. After the final step, the die was assembled and removed from the dry box or cold room and the sample mixture was pressed under a total pressure of 10 tons for 5 minutes. This produced a KBr disc about 2 millimetres thick and 12 millimetres in diameter. The modification was necessary in order to facilitate removal of the KBr disc from the die

[1] U. SCHIEDT and H. REINWEIN *Z. Naturforsch.* **76**, 270 (1952).
[2] M. M. STIMSON and J. O'DONNELL *J. Amer. Chem. Soc.* **74**, 1805 (1952).
[3] F. A. MILLER and C. H. WILKINS *Anal. Chem.* **24**, 1253 (1952).
[4] A. R. PHILPOTTS and W. THAIN *Anal. Chem.* **24**, 638 (1952).
[5] G. J. MINKOFF *Proc. Roy. Soc.* **A224**, 176 (1954).
[6] H. R. WILLIAMS and H. S. MOSHER *Anal. Chem.* **27**, 517 (1955).

and also aided in preventing atmospheric attack upon the sample during the scan with the Baird Associates, Model B, infra-red spectrophotometer. Rock-salt optics were employed in the spectrophotometer for the region of scan from 2–16 microns (5000 cm^{-1} to 625 cm^{-1}).

RESULTS

The spectra of Li_2O_2, Na_2O_2, $Na_2O_2 \cdot 8H_2O$, and $Na_2O_2 \cdot 8D_2O$ are reproduced in Fig. 1. They show: (1) the cut off at long wavelengths for lithium peroxide to be about 10–12 microns (1000 cm^{-1}–840 cm^{-1}), (2) water and carbonate bands for all the samples (carbonate content is approximately 2% in all the samples except for the

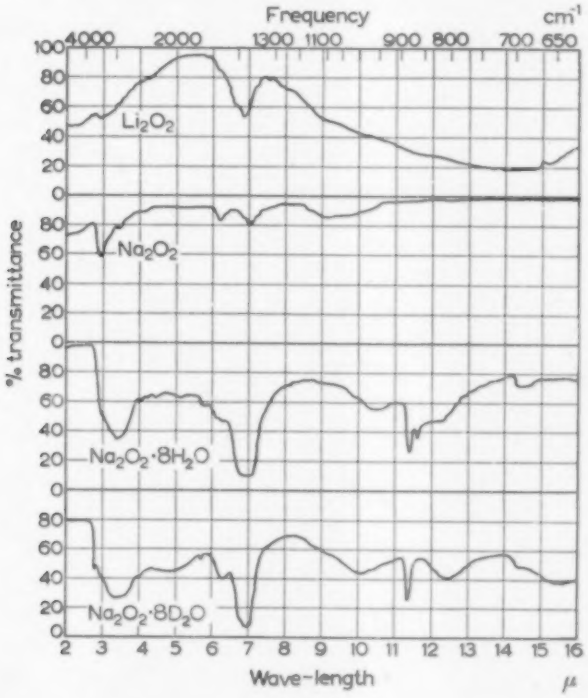

FIG. 1.

Na_2O_2 sample, where it is much less), (3) a small absorption band at 11·6 microns (862 cm^{-1}) which appears only occasionally in the spectra of peroxide hydrate samples.

DISCUSSION

The spectra show no characteristic sharp bands for peroxide and superoxide, O_2^{-2} and O_2^{-1}, which is consistent with the theory that both peroxide and superoxide ions are homopolar, and thus their vibrations are infra-red inactive. The major impurities are indicated to be water and carbonate, except for the hydrate samples where water is already combined with the sample. GIGUERE[7] states that no bands were observed in the rock salt region for a superoxide (KO_2) sample, but upon short exposure to damp air nearly a dozen bands were brought out belonging to the carbonate, hydroperoxide,

[7] P. A. GIGUERE and K. B. HARVEY *J. Amer. Chem. Soc.* **76**, 5891 (1954).

and possibly other ions. He further states that the characteristic frequency of the peroxide group at 880 cm^{-1} became prominent under such conditions. However, since the breathing type (ν_2) vibration for carbonate ($CO_3^{=}$) also appears at this same frequency of 879 cm^{-1},[8] it is believed that if the peroxide band is present at all, it would be either partially or completely masked by the sharp characteristic band for carbonate. This fact is borne out through observation of the accompanying spectra. In addition, absorption bands in the region 800–925 cm^{-1} have been attributed to "co-ordinated" water in other systems.[9]

Thermal decomposition studies indicate that the actual structural units in $Na_2O_2 \cdot 8H_2O$ might be $2NaOH \cdot H_2O_2 \cdot 6H_2O$,[10] but the absence of strong bands in the spectra of peroxide hydrate samples other than water and carbonate spreads some doubt upon this possibility. No indication of a possible existence of an O_3^{-1} ion was observed in any of the spectra. An explanation for the appearance of the 11·6 micron (862 cm^{-1}) band in a few of the hydrate samples is unknown, although it could involve a crystal structure effect in $CO_3^{=}$. Difficulties encountered with sample handling make it hard to investigate the exact nature of this band.

We wish to acknowledge the aid of RICHARD TALLMAN in preparing the Na_2O_2 sample, Dr. WILLIAM H. SCHECHTER of the Callery Chemical Company for supplying samples of NaO_2 and KO_2, and Dr. A. PAVLIK JR. of Barium Chemicals, Inc., for supplying samples of lithium, strontium, and barium peroxides.

[8] G. HERZBERG *Infra-red and Raman Spectra of Polyatomic Molecules* D. Van Nostrand, New York, 1945, page 178.
[9] J. FUJITA, K. NAKAMOTO, and M. KOBAYASHI *J. Amer. Chem. Soc.* **78**, 3963 (1956).
[10] (a) S. Z. MAKAROV and N. K. GRIGOR'EVA *Izvest. Akad. Nauk. S.S.S.R., Otdel. Khim. Nauk.* 1955, 17–20 (*C.A.* **49**, 12942b and 15419f).
(b) S. H. COHEN and J. L. MARGRAVE Unpublished work (1956).

J. Inorg. Nucl. Chem., 1957, Vol. 4, pp. 93 to 99. Pergamon Press Ltd., London

THE DISTRIBUTION OF PLUTONIUM AND FISSION PRODUCTS BETWEEN MOLTEN URANIUM AND MOLTEN URANIUM TRIFLUORIDE-BARIUM HALIDE MIXTURES

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Abstract—The distribution of plutonium between molten uranium and mixtures of uranium trifluoride with barium chloride or fluoride has been measured at temperatures of 1200–1400°C. The equilibrium constant for the reaction $Pu + UF_3 = PuF_3 + U$ is found to be $72 \pm 50\%$, calculated on a mole fraction basis. This corresponds to a standard free energy change for the reaction at 1200°C of approximately −13 kcals, which agrees well with the estimated value.

On the 20-g-of-uranium scale, at least 60-min contact between phases is required to establish equilibrium. Fission-product removals from the metal are greater than 99% under a variety of conditions, but owing to the complications of self-slagging effects, the results cannot be interpreted in terms of equilibrium constants. About 80% of fission-product caesium and about 20% strontium volatilizes under these conditions.

The same final equilibrium is achieved if the salt mixtures are initially made up with uranium tetrafluoride instead of the trifluoride, reduction by the metallic phase being substantially complete.

A NUMBER of workers have reported preliminary investigations of the extraction of plutonium from uranium by molten salts.[1–3] The basic reaction involved is $xPu(U) + 3MY_x \rightleftharpoons xPuY_3 + 3M(U)$, where M is a metal of valency x and Y is chloride or fluoride. Salts which have been used include the fluorides and chlorides of the alkali and alkaline earth metals, and of uranium. Uranium fluoride is the preferred reagent in some cases, since the reaction product, uranium metal, causes no contamination of the bulk metal phase.

It was the original intention in this work to study the extraction of plutonium by molten uranium tetrafluoride mixtures; however, in the presence of a molten uranium metal phase, virtually complete reduction to the trivalent state was found to occur. Consequently, we have studied the equilibrium between molten uranium and uranium trifluoride. The same final equilibrium is achieved whether mixtures are made up with the tetrafluoride or with the trifluoride. We have found uranium trifluoride to be quite stable at temperatures up to 1400°C in the presence of uranium metal. The pure trifluoride disproportionates at high temperatures, but even at 1500°C we have found that the rate of disproportionation leads to only about 20% decomposition in 30 min in the absence of a metallic phase.

Recent studies on self-slagging effects[4] have confirmed that plutonium is relatively unaffected by the presence of normal production impurities (C, N, O) when uranium containing trace-plutonium is melted. It is therefore legitimate to assume that the distribution of plutonium between salt and metal phases represents a single

[1] E. E. MOTTA *Progress in Nuclear Energy III:* Process Chemistry **1**, p. 309; Pergamon Press, London (1956).
[2] A. M. AIKIN and D. E. MACKENZIE *ibid.* p. 316 (1956).
[3] F. S. MARTIN and G. L. MILES *ibid.* p. 329 (1956).
[4] F. S. MARTIN and E. W. HOOPER A.E.R.E. C/R 2059 (1956).

equilibrium, and calculations may be made accordingly. This is not the case with fission products, where extraction into the salt phase results from a combination of oxidation by the salt, and solution of fission-product slag by the melt. The only prediction that may safely be made with respect to fission products is that their removal should be at least as extensive as in any self-slagging operation, and that, as usual, the noble metals such as ruthenium will be unaffected.

Although pure barium halides may extract plutonium from molten uranium,[4] the equilibrium constant for the reaction is low (approx. 10^{-8} at 1500°K). In barium halide mixtures containing uranium trifluoride, reaction of plutonium with the latter may safely be assumed to be the one controlling equilibrium, since the equilibrium constant in this case is very much greater than unity.

EXPERIMENTAL

The resistance-wound furnace, general apparatus, and procedure previously described[3] were used. Melts were prepared by mixing appropriate quantities of uranium trifluoride or Springfields standard production uranium tetrafluoride (dried at 120°C in air) with barium chloride or fluoride (dried at 800°C in air). Alumina crucibles were used. Neutron-irradiated uranium metal containing about 50 μg/g of plutonium was used for equilibrations, which were carried out under 1 atm of pure argon. During the equilibrations, the molten salt was allowed to float on top of the molten metal, the interfacial area being identical for all runs. No mechanical stirring was carried out.

Preparation of uranium trifluoride. The method used was adapted from one described by WARF[5] in which finely divided uranium metal was allowed to react with the stoichiometric quantity of uranium tetrafluoride at 1100°C. The product was shown by X-ray analysis to be >98% UF_3 with traces of UO_2.

Analysis of samples. After a run, crucibles were cracked with a hammer (using closed plastic bags to avoid dust-ingestion hazard) and the salt phase was separated mechanically from the metal billet. The latter was usually obtained with a bright smooth surface. Salt phases were analysed for plutonium and fission products after total dissolution, whereas the billets were dissolved skinwise to obtain an idea of plutonium distribution. In an attempt to obtain mass balances, used crucibles were digested in fused carbonate, fused bisulphate, or hot strong nitric acid, and the leachings analysed.

RESULTS AND DISCUSSION

Plutonium distribution. The attainment of equilibrium was tested by examining the variation of extraction of plutonium with time. Table 1 shows that, on the scale of about 20 g of metal containing 50 μg/g of plutonium, heating for half an hour is insufficient; equilibrium may be almost reached in 1 hour, and is certainly reached in 1½ hours. This behaviour is reflected in the plutonium-concentration profiles through the billets. Fig. 1 shows this for two of the runs quoted in Table 1. The distribution profile is almost horizontal for the 90-min run, but shows a pronounced gradient for the 30-min run. The high concentrations at the surface in each case are due to the occlusion of small amounts of salt phase in the skin of the billet. The fact that the concentration rises towards the centre of the billet shows that there has been little stirring by convection and that the attainment of equilibrium is controlled mainly by diffusion to the interface. Although only two profiles are shown here by way of example, they were in fact determined for all samples. Where a profile was not horizontal, owing to some circumstance having limited the time of equilibration to less than about 1 hour, the concentration value at the lowest point of the profile was taken as being the nearest approximation to the equilibrium value.

[5] J. C. WARF A.E.C.D. 2413 (1948).

TABLE 1.—VARIATION OF PLUTONIUM EXTRACTION WITH TIME

Wt. ratio metal/salt = 2·0

Composition of salt: $N_{UF_3} = 0{\cdot}469$, $N_{BaCl_2} = 0{\cdot}531$

Temp. (°C)	Time (min)	% Pu extracted from core of billet
1200	30	87·0
	60	90·0
	90	95·5
	120	95·0
1300	30	80·0
	60	96·6
	90	98·3
	120	98·3

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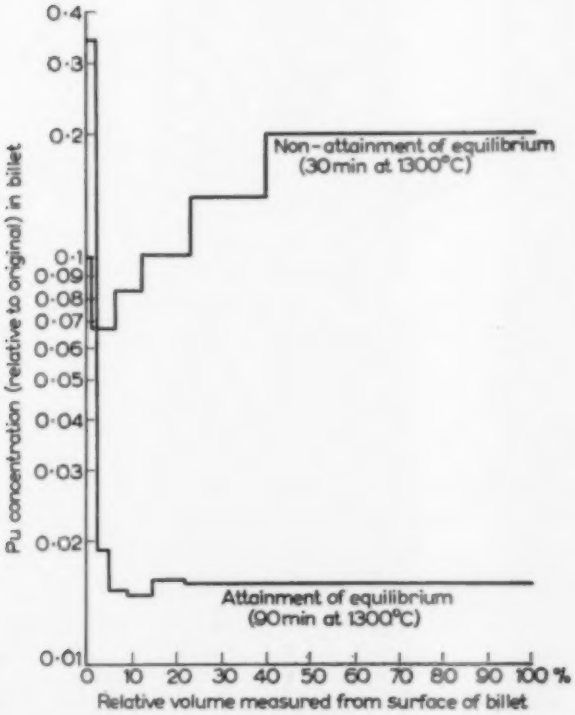

FIG. 1.—Radial distribution of plutonium through a uranium billet after contact with fused UF_3—$BaCl_2$.

The amount of plutonium extracted at a variety of salt compositions and phase ratios is shown in Table 2. In this table, UF_3 mole fractions have been calculated on

TABLE 2.—EQUILIBRIUM CONSTANTS FOR THE DISTRIBUTION OF PLUTONIUM BETWEEN MOLTEN URANIUM AND MOLTEN URANIUM TRIFLUORIDE MIXTURES

Temp. (°C)	Wt ratio metal/salt total	Mole ratio metal/salt total	N_{UF_3} in salt	Second salt component	% Pu extracted	K	Mean K
1200	2	1·75	0·0	$BaCl_2$	42		72
		1·80	0·0905		84	96	
		1·84	0·181		88	75	
		2·03	0·469		96·3	113	
		2·21	0·726		93	40	
		2·48	1·00		99·35	(378)	
	4	3·32	0·0905	$BaCl_2$	57	49	
		3·69	0·181		76	65	
		4·05	0·469		97·8	38	
	6	4·98	0·0905	$BaCl_2$	54	65	
		5·54	0·181		78	109	
		6·08	0·469		85	74	
1300	2	2·03	0·469	$BaCl_2$	98·3	250	213
		2·21	0·726		98·3	176	
	2	1·47	0·0	BaF_2	35		65
		1·70	0·33		92·7	65	
1350	2	1·47	0·0	BaF_2	69		
1400	2	1·70	0·33	BaF_2	93·2	70	70

the basis of complete reduction of added UF_4, except, of course, where UF_3 was added as such. As would be expected on general grounds, plutonium extraction decreases as the relative volume of the salt phase decreases, and as the mole ratio of uranium trifluoride in the latter decreases.

The reaction representing extraction is

$$Pu(U) + UF_3(BaX_2) \rightleftharpoons PuF_3(BaX_2) + U$$

and the equilibrium constant in terms of mole fractions is

$$\frac{N_{PuF_3} \cdot N_U}{N_{Pu} \cdot N_{UF_3}} = K$$

If % Pu represents the plutonium extracted from the metal into the salt, then

$$\left(\frac{\%\ \text{Pu}}{\text{total salt moles}}\right) \Big/ \left[\frac{(100 - \%\ \text{Pu})}{\text{moles of U}} \cdot N_{UF_3}\right] = K$$

since N_U is virtually unity. Therefore

$$K = \frac{\%\ \text{Pu}}{100 - \%\ \text{Pu}} \cdot \frac{\text{moles of U}}{\text{total salt moles}} \cdot \frac{1}{N_{UF_3}} \qquad (1)$$

Values of K, calculated from equation (1) are given in Table 2. Apart from two values for the barium chloride mixture at 1300°C, there is a fair degree of consistency among the values; the spread among the values at 1200°C is represented by $K = 72 \pm 50\%$. The main causes of scatter are probably lack of attainment of equilibrium in a few experiments, and crucible attack leading to oxide contamination of the melts. The equilibrium constant was also calculated using salt-phase activities calculated from the equation

$$RT \ln A_{M_1X_1} = RT \ln (N_{M_1}N_{X_1}) + N'_{M_2}N'_{X_2}\,\Delta G^{\circ}_{M_2X_2}$$

given by FLOOD *et al.*[6] However, the results showed far greater divergence than those calculated on a simple mole fraction basis. This probably indicates fairly ideal mixing of UF_3 with $BaCl_2$ or BaF_2. X-ray examination of the mixed salts seems to support this. The fused mixture of $UF_3 + BaCl_2$ shows no evidence of compound formation, nor are the lattices of UF_3 or $BaCl_2$ distorted in any way. The fused mixture of $UF_3 + BaF_2$ again shows no evidence of compound formation, but the BaF_2 and UF_3 lattices show slight distortion due to solid solution.[7]

Using the value $K = 72$, the standard free energy change for the reaction $UF_3 + Pu = PuF_3 + U$ at 1200°C is calculated to be 12·8 kcal. This is close to the value of 12 kcal derived from estimated thermal data.[8]

In an experiment not reported in Table 2, a metal billet was extracted twice with successive salt phases at 1200°C, the metal-salt weight ratio being 2 : 1 and the mole fraction of $UF_3 = 0{\cdot}469$. The total plutonium extraction was 99·9% as compared with 96·3% for the single extraction. In another run, an extraction was carried out on irradiated metal which had been melted and recast, thus removing reactive fission products by self-slagging. Within experimental error, the result was similar to that using unslagged metal.

Fission product extraction. In all runs the phases were analysed for gross β and γ activities. In the majority of runs they were also analysed for strontium and cerium and in a minority for caesium. The equilibrium results are presented in Table 3. Concentration profiles were also determined as for plutonium, but in almost every case they were flat.

In most cases, the presence of a high concentration of fission products in the skin was observed; the solution of fission-product slages in halide fluxes is a slow process.

The fact that fission-product removals (Table 3) may approach 100% indicates that there is considerable reaction beyond that of self-slagging, which usually only removes 80–90% of the fission products. Little effect is expected for the more noble elements such as ruthenium, and these were not analysed for. The results of experiment 14 (Table 3) are interesting in that metal which had previously been self-slagged and cast was used. The efficiency of removal of residual fission products is low.

[6] H. FLOOD, T. FÖRLAND, and K. GRJOTHEIM *Z. anorg. Chem.* 276, 289-315 (1954).
[7] R. W. M. D'EYE and F. S. MARTIN A.E.R.E. C/M 292 (1956).
[8] F. S. MARTIN and G. L. MILES *Progress in Nuclear Energy III:* Process Chemistry I, p. 294, Pergamon Press, London (1956).

TABLE 3.—THE EXTRACTION OF FISSION PRODUCTS FROM MOLTEN URANIUM BY MOLTEN HALIDES

Serial	Temp. (°C)	Wt. ratio metal/total salt	N_{UF_3} in salt	Second salt component	% removal				
					Gross $\beta\gamma$	Gross γ	Sr	Ce	Cs
1	1200	2	0·0	$BaCl_2$	93	93			
2			0·0905		92	92		89	
3			0·181		92	92	98·3	84	97
4			0·469		97·1	95·3	99·9	99·9	
5			0·726		95·7	94·8			
6			1·00		93	98·5			
7		4	0·0905	$BaCl_2$	89	90		83	
8			0·181		89	95	97·2		
9			0·469		94	93	99·6	95·2	>99
10		6	0·0905	$BaCl_2$	87	89	96·6	73	
11			0·181		92	90	97	85	
12			0·469		93	92	97·9	91	96
13		2 × 2 (see note a)	0·469	$BaCl_2$	98·1	97	99·9	>99·9	
14		2 (see note b)	0·469	$BaCl_2$	60	66	45	60	
15	1300	2	0·469	$BaCl_2$	97·2	95·3	99·79	99·2	>99
16			0·726		97·4	96	>99·9	>99·9	
17		2	0·0	BaF_2	96	94	98	85	
18			0·33		97·3	95·8	99·3	99·3	
19	1350	2	0·0	BaF_2	97·6	96·1	99·8		
20	1400	2	0 33	BaF_2	97·6	96·4	99·3	99·2	

Note: (a) Serial 13 represents extraction by two successive batches of salt, the first batch being mechanically removed before addition of the second batch.
(b) Serial 14 was carried out on metal which had previously been melted and some of the reactive fission products removed by self-slagging.

In the case of gross β and γ activities, this is because a larger proportion of the activity must be due to unreactive noble fission products; in the case of the reactive metals, strontium and cerium, it must be because these residual amounts are present as insoluble or unreactive slag which was too finely dispersed to be removed by flotation and casting.

Many mass balances were determined. For cerium these were usually 90–95%, for strontium 70–80%, and for caesium about 20%. Allowing for active material

retained by the crucible, this means that little cerium was lost by volatilization; about a fifth of the strontium and four-fifths of the caesium were lost even though the equilibrations were carried out under 1-atm pressure of argon.

The fission-product extraction data cannot be used to calculate equilibrium constants, because of the complicating effects of self-slagging.

CONCLUSIONS

Using the average value of the equilibrium constant for the plutonium-uranium trifluoride reaction, $K = 72$, we have calculated the ideal curves relating plutonium extraction to relative phase volume and composition at 1200°C. They are given in Fig. 2. The binary mixture UF_3—$BaCl_2$ has been chosen as an example rather than UF_3—BaF_2, for practical reasons, on account of the lower melting-points of the former system; it is also more readily dissolved in aqueous media should this be necessary.

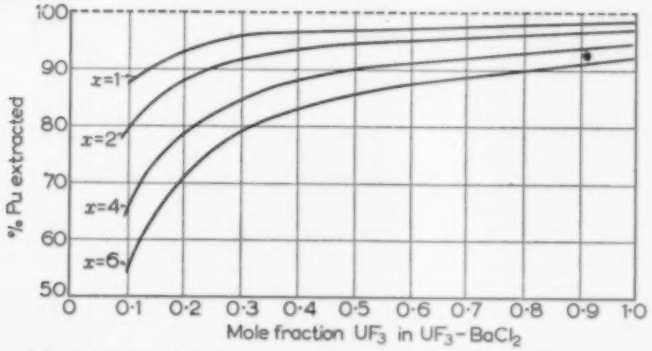

FIG. 2.—Calculated extraction of plutonium from uranium by UF_3—$BaCl_2$ mixtures at 1200°C
X = mole ratio metal phase/salt phase.

The curves in Fig. 2 show that, whatever the relative volumes of metal to salt phases are, there is not much point in increasing N_{UF_3} beyond about 0·4 from the point of view of plutonium extraction. In addition, it is easily shown that it is preferable to carry out a multi-stage extraction with a small amount of salt phase than one extraction with a corresponding larger quantity. For example, when $x = 6$ and $N_{UF_3} = 0{\cdot}4$, % Pu = 83 for one stage and 97·1 after the second stage, giving an overall concentration factor for plutonium with respect to uranium of $(0{\cdot}97/2) \times (6/0{\cdot}4) = 7{\cdot}3$. About the same overall extraction of plutonium is gained by a single extraction when $X = 1$ and $N_{UF_3} = 0{\cdot}4$. Here, however, the concentration factor with respect to uranium is only $0{\cdot}97 \times 1/0{\cdot}4 = 2{\cdot}4$, about one-third of the value in the former case.

Acknowledgements—We thank Dr. R. W. M. D'EYE for X-ray analysis and Mr. G. J. HUNTER and others for radiochemical analysis.

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TRI-*n*-BUTYL PHOSPHATE AS AN EXTRACTING SOLVENT FOR INORGANIC NITRATES—I

ZIRCONIUM NITRATE

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(*Received* 16 *October* 1956)

Abstract—The extraction of tracer zirconium by 19% v/v (0·69 M) tri-*n*-butyl phosphate (TBP) in kerosene has been studied from aqueous solutions consisting of (i) nitric acid, (ii) nitric acid *plus* an inextractable nitrate (sodium nitrate), and (iii) nitric acid *plus* an extractable nitrate (uranyl nitrate). The partition coefficients increase steeply with rising acidity, they are little affected by substitution of sodium nitrate for nitric acid, and they fall considerably on addition of uranyl nitrate to the system.

THIS is the first of a group of papers dealing with the extraction by tri-*n*-butyl phosphate (TBP) of the nitrates of elements which are of interest to the atomic energy programme. Zirconium is of particular importance because it is one of the most readily extractable of the longer-lived fission products, and is therefore one which frequently contaminates thorium, uranium or plutonium salts prepared by solvent extraction.

This paper is based on an earlier A.E.R.E. report.[1] It is intended to discuss the physical chemistry fully elsewhere.

EXPERIMENTAL

Preparation of Zr^{95} tracer

The tracer used was prepared from a solution of fission products in nitric acid by extraction first into 19% TBP in kerosene from 8 M HNO_3, followed by backwashing into water, and then into 0·05 M TTA (thenoyltrifluoracetone) in benzene from 1 M HNO_3. The resulting TTA solution was left standing over 1 M HNO_3. When a specimen of Zr^{95} was required, the phases were stirred for 30 min to extract the Nb^{95} daughter, which is also radioactive. The Zr^{95} was then extracted into 8 M HNO_3. Traces of TTA were eliminated by scrubbing with benzene followed by air-sparging. The solution was normally used the same day to avoid too much growth of Nb^{95}.

Purity of TBP

The TBP was generally purified by the method described by ALCOCK, GRIMLEY, HEALY, KENNEDY, and MCKAY.[2] A few comparative experiments with material which had merely been washed with alkali and water revealed the inadequacy of this method of treatment; the aqueous phase was 5·1 M HNO_3 and the TBP was diluted to 19% in kerosene:

[1] H. A. C. MCKAY, W. H. HARDWICK, and F. C. BEDFORD A.E.R.E. C/R 923 (1952).
[2] K. ALCOCK, S. S. GRIMLEY, T. V. HEALY, J. KENNEDY, and H. A. C. MCKAY *Trans. Faraday Soc.* **52**, 39 (1956).

	Tracer initially in aqueous phase				Tracer initially in organic phase		
	Partition coefficient (org/aq) after				Partition coefficient (org/aq) after		
	15 min	45 min	90 min	120 min	30 min	60 min	90 min
Pure TBP	0·41	0·46	0·46	—	0·58	0·52	0·58
Alkali-washed TBP	0·85	1·10	—	1·22	1·58	1·81	1·91

The much better agreement of the forward and backward partitions and the lack of a drift with time, demonstrate the superiority of the more highly purified solvent.

Dilution of TBP

The work reported here was nearly all carried out with 19% v/v (0·69 M) TBP in "odourless" kerosene.

Partition measurements

Partition coefficients were determined by stirring *ca.* 5 ml of each phase together in a centrifuge tube for about 30 min, centrifuging, and separating the phases for analysis. It later became apparent that 5 min stirring is usually ample and that centrifuging can be dispensed with, and in subsequent papers in this series the procedure was simplified accordingly. The solutions were not thermostated in the present work, but the ambient temperature was fairly constant at 20–23°C.

The Zr^{95} concentrations used were generally in the range 10^{-11} to 10^{-12} M. At these levels the formation of polynuclear species by hydrolysis is unlikely to be important,[3] but radiocolloids involving trace impurities might still cause difficulties. For this reason we used a highly acid zirconium stock solution (8 or 10 M HNO_3), and only exposed the zirconium to lower acidities for the duration of the actual experiment. Furthermore in the experiments with nitric acid, the zirconium was first extracted into 19% TBP, and the partition coefficients were determined by equilibrating this TBP phase with various aqueous phases. Inextractable species in the original aqueous solution would be eliminated by this back extraction procedure. PEPPARD, MASON, and MAIER[4] used a similar procedure, back-extracting twice and comparing the two results obtained.

In the experiments with added sodium or uranyl nitrate the TBP phase was conditioned to approximately the equilibrium acidity and uranyl nitrate concentration by shaking with several (e.g. four) successive volumes of the aqueous phase, with no zirconium tracer present. The tracer was then added, in 8 or 10 M HNO_3, to further aqueous phase, and a final equilibration was carried out.

Zirconium analyses were carried out by γ-counting, nitric acid analyses by alkali titration, and uranium analyses colorimetrically by the peroxide method.

RESULTS and DISCUSSION

Extraction from nitric acid solutions

The results obtained with 19% TBP in kerosene are given in Table 1.

The extraordinary rise in the partition coefficient at high acidities was quite unexpected and it seemed advisable to test whether it could be due to trace impurities. A measurement was therefore made at an acidity of 11·4 M in the presence of 0·001 M inactive zirconium; this is still effectively a trace concentration, yet it should greatly

[3] J. S. JOHNSON and K. A. KRAUS *J. Amer. Chem. Soc.* **78**, 3937 (1956); A. J. ZIELEN and R. E. CONNICK *ibid.*, p. 5785.
[4] D. F. PEPPARD, G. W. MASON, and J. L. MAIER *J. Inorg. Nucl. Chem.* **3**, 215 (1956).

TABLE 1

HNO_3 conc. (aq)	0·98	2·02	2·25	3·01	4·01	4·96	5·19	6·04	6·94 M
Partition coeff. (org/aq)	0·015	0·045	0·051	0·120	0·23	0·49	0·53	0·90	1·37

HNO_3 conc. (aq)	7·98	8·03	9·1	10·2	10·5	11·2	12·2	13·1 M
Partition coeff. (org/aq)	2·37	2·02	4·4	8·2	9·8	11·4	40	134

minimize the effect of trace impurities. The figure obtained was 19·5, compared with 21 interpolated from the data at tracer levels. In a further experiment, three successive backwashes were carried out at 11·6 M HNO_3, giving partition coefficients of 43, 46, and 51 respectively; these are reasonably constant, though on the high side.

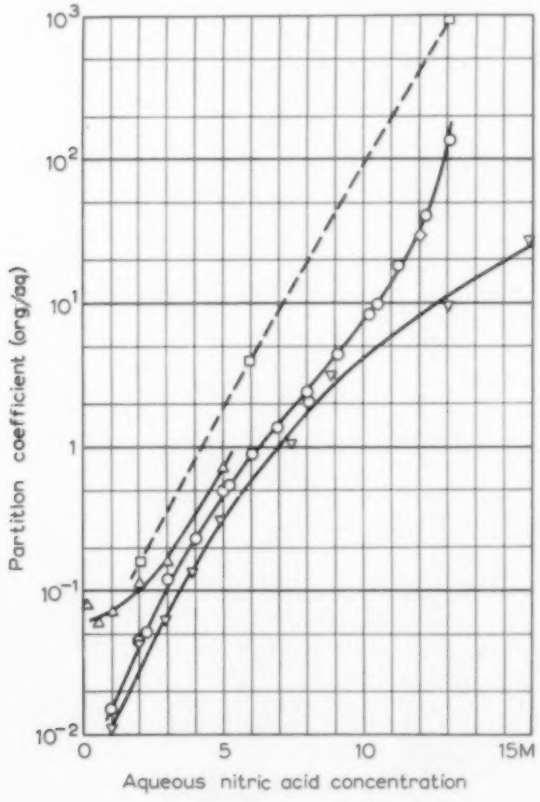

FIG. 1.
○ Our data, 19% TBP in kerosene.
▽ MURBACH and MCVEY,[5] 30% TBP in CCl_4.
△ BRUCE,[6] 15% TBP in Varsol.
□ PEPPARD, MASON, and MAIER,[4] 100% TBP.
◇ Ditto, 25% TBP in benzene.

Results by other authors[4–6] are compared with ours in Fig. 1. It is a little surprising that the extraction does not always increase with increasing TBP concentration; presumably this is due to the different diluents used.

The present authors also obtained some results at greater dilution of the TBP in kerosene. The partition coefficient varied approximately with the square of the TBP percentage, indicating the formation of $Zr(NO_3)_4 \cdot 2TBP$. The original experimental basis for this conclusion has, however, been criticized by MURBACH and MCVEY,[5] and a new series of measurements extending to lower TBP concentrations has therefore

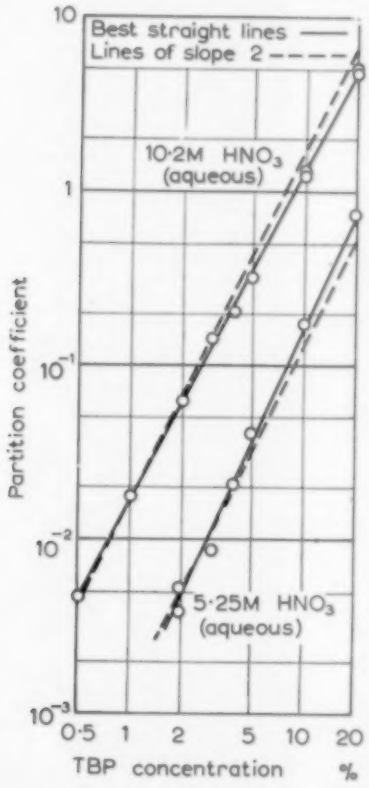

FIG. 2.

been made by HESFORD[7] at 25°C, with the results shown in Fig. 2 (which are probably of rather greater accuracy than our earlier results). The best lines through all the points in Fig. 2 are of slopes 2·2 at 5·25 M HNO_3 and 1·9 at 10·2 M HNO_3. In our view this implies, without much doubt, a square law in the limit at low TBP concentrations (say $<1\%$ in kerosene), with deviations from this law at higher TBP concentrations due to nonideality of the organic phase. It certainly seems improbable that the limiting law would be for instance a cubic.

[5] E. W. MURBACH and W. H. MCVEY U.S.A.E.C. LRL—115 (1954).
[6] F. R. BRUCE *Peaceful Uses of Atomic Energy*, Vol. 7 (United Nations, New York, 1956) Paper P/719.
[7] E. HESFORD Private communication.

It is interesting to note that LEVITT and FREUND[8] found a similar square law in chloride solutions, and deduced the formation of $ZrCl_4 \cdot 2TBP$.

Extraction in presence of sodium nitrate

Our results with 19% TBP in kerosene are given in the accompanying table. The sodium nitrate itself is almost inextractable.

TABLE 2

Concentrations			Partition coefficient (org/aq)	
HNO_3 (aq)	$NaNO_3$ (aq)	HNO_3 (org)		
1·00 M	0·0 M	0·115 M	0·015	
0·99	1·0	0·205	0·05	(0·045)
0·99	2·0	0·27	0·12	(0·12)
0·99	3·0	0·33	0·25	(0·23)
0·99	4·5	0·41	0·64	(0·65)
0·99	6·0	0·48	1·41	(1·40)
2·00	0·0	0·28	0·045	
2·00	1·0	0·37	0·14	(0·12)
2·00	2·0	0·42	0·26	(0·23)
2·00	3·0	0·47	0·48	(0·49)
1·98	4·0	0·51	0·66	(0·89)
1·98	4·5	0·54	0·74	(1·12)
1·98	5·0	0·56	1·06	(1·40)

The figures in brackets in the last column of Table 2 are the partition coefficients in presence of nitric acid only (taken from Fig. 1) at the same nitrate ion concentrations as in the mixtures with sodium nitrate. In most cases the two partition coefficients are very similar. This means that the controlling factor is the total nitrate ion concentration. With other elements there is always a rise in extraction when sodium nitrate replaces nitric acid; the absence of such a rise with zirconium may be due to hydrolysis, which is considerable even at acidities of 1–2 M.[3,9]

Extraction in presence of uranyl nitrate

Uranyl nitrate differs from sodium nitrate in being itself extractable into TBP, and its presence in the organic phase reduces the amount of free solvent and hence the extraction of zirconium. Our results with 19% TBP in kerosene are given in Table 3. At *ca.* 2 M HNO_3 the ratio of the partition coefficients for zirconium and uranium is approximately constant. This arises because each nitrate forms a complex incorporating two molecules of solvent, so that both partition coefficients depend on the square of the amount of free TBP, i.e. the amount not combined with either nitric acid

[8] A. E. LEVITT and H. FREUND *J. Amer. Chem. Soc.* **78**, 1545 (1956).
[9] R. E. CONNICK and W. H. MCVEY *J. Amer. Chem. Soc.* **71**, 3182 (1949).

TABLE 3

Concentrations				Partition coefficient (org/aq)		
HNO_3 (aq)	$UO_2(NO_3)_2$ (aq)	HNO_3 (org)	$UO_2(NO_3)_2$ (org)	Zirconium	Uranium	Ratio
2·00 M	0·000 M	0·28 M	0·000 M	0·045	—	—
1·97	0·0235	0·15*	0·156	0·0185	6·6	0·0028
1·97	0·086	0·11*	0·24	0·0072	2·8	0·0026
1·98	0·21	0·07*	0·30	0·0047	1·44	0·0033
5·00	0·000	0·61*	0·000	0·55	—	—
5·02	0·0045	0·44*	0·099	0·50	22	0·023
5·12	0·087	0·15*	0·27‡	0·134	3·1	0·043
5·37	0·32	0·03*	0·35	0·076	1·07	0·071
4·95	1·01	0·02*	0·36‡	0·024	0·35	0·069

* Estimated from other data.
‡ By difference.

or uranyl nitrate. At *ca.* 5 M HNO_3 there are too many complications for this simple proportionality to hold.

The authors wish to express their thanks to Dr. J. M. FLETCHER, under whose general direction this work was carried out.

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A COMPARATIVE STUDY OF POLYOL COMPLEXES OF ARSENITE, BORATE, AND TELLURATE IONS*

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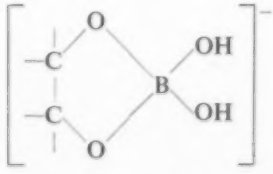
(*Received* 4 *October* 1956)

Abstract—An investigation using a pH method has been made of the polyol complexes of arsenite, borate, and tellurate ions. The constants obtained for arsenite and borate ions correlate well. The order of values for tellurate complexes does not agree, however, with that for the other two ions; evidence is presented which indicates that the variations in order are caused by steric effects.

THE formation of complexes between the borate ion and polyhydroxylic compounds (polyols) is well established. BIOT[1] in 1842 reported that a solution of boric acid became acid to litmus when various sugars were added; in the following years, many workers tested series of polyols to study their effects on the acidity of boric acid. For example, BÖESEKEN and VAN ROSSEM[2] made a conductimetric study of the reactions of boric acid with glycerol, catechol, resorcinol, pyrogallol, and mannitol. Other studies of polyol-borate complexes include many[3–9] that give quantitative data.

BÖESEKEN[10] has recently summarized much of the work on borate complexes with sugars.

HERMANS[11] reported that diols of *cis* configuration often formed two types of complexes which could be isolated. One is formed by splitting out two molecules of water from a polyol molecule and a borate ion, while the other is formed by splitting out four water molecules from glycol molecules and a borate ion. Their structures presumably are of the types



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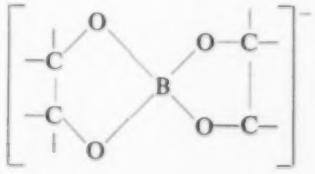

with oxygens in tetrahedral arrangement about the boron atom.

* Taken from portions of the M.S. and Sc.B. theses of G. L. R. and A. L. L., respectively. A part of this work was supported by the Office of Ordnance Research of the U.S. Army.

[1] M. BIOT *Compt. rend.* **14,** 49 (1842).
[2] J. BÖESEKEN and A. VAN ROSSEM *Rec. trav. chim.* **30,** 392 (1912).
[3] J. BÖESEKEN (a) *Ber.* **46,** 2612 (1913); (b) *Chem. Zentr.* **314,** 2778 (1924).
[4] J. BÖESEKEN and N. VERMAAS *Rec. trav. chim.* **54,** 853 (1935).
[5] S. M. MEHTA and K. V. KANTAK *J. Amer. Chem. Soc.* **74,** 3470 (1952).
[6] H. SCHAFER *Z. Anorg. Chem.* **247,** 96 (1941).
[7] L. THUNG and H. CHANG *J. Chinese Chem. Soc.* **9,** 125 (1942).
[8] G. MAGNANINI (a) *Z. physik. Chem.* **6,** 58 (1890); (b) *Gazz. Ital.* **11,** 8 (1891).
[9] Y. TSUZUKI and Y. KIMURA *Bull. Chem. Soc. Japan* **15,** 27.
[10] J. BÖESEKEN *Advances in Carbohydrate Chemistry* Vol. 4, pp. 189-210. W. W. PIGMAN and M. L. WOLFRAM, Eds. Academic Press, New York (1949).
[11] P. H. HERMANS *Z. anorg. Chem.* **142,** 83 (1925).

There are some recent quantitative studies of the mannitol-borate system.[12–15] The data, which has been summarized by ANTIKAINEN,[14] indicates the borate ion can complex with either one or two molecules of mannitol. In view of the other complications found here (vide infra), it is hardly surprising that there is some disagreement as to the correct values of the constants. There now seems to be general agreement, however, that the borate ion is the complexing species rather than boric acid.

Complexes between arsenite ion and polyols are known.[16] Using colorimetric pH measurements, ENGLUND[17] studied the combination of arsenite with mannitol and sorbitol.

Although it has been known for years that glycerol enhances the acidity of telluric acid,[18] no quantitative study of complexing has been made. FOUASSON[19] made measurements on the ionization constants of telluric acid in the presence of glycerol, mannitol, and two glucoses. An investigation of the alkalimetric determination of telluric acid in the presence of polyols has been carried out.[20] Since the submission of this paper, it has come to our attention that ANTIKAINEN[20a] has initiated a series of studies on the polyol complexes of tellurate ion.

In view of the need for more data on polyol complexes of these anions, this comparative study was made. Formation constants for the complexes have been determined by a pH method, and the values have been compared using the method of linear free energy relations.

EXPERIMENTAL

Reagents. Most of the polyols were Eastman Kodak white-label grade and were used without further purification. Phenyl-1, 2-ethanediol (practical) was recrystallized from benzene and hexane, and 2,3-butanediol (practical) was distilled under vacuum. The polyvinylalcohol (Elvanol grade 70-05), which was donated by the Electrochemicals Department of E. I. du Pont de Nemours and Co., was used without further purification; its water solution was found to be neutral.

Borax and arsenious acid were reagent grade and the sodium hydroxide was Reagent Special (low carbonate). The telluric acid either was prepared in this laboratory by permanganate oxidation of tellurium dioxide[21] or was obtained from Fisher Scientific Co. At least four recrystallizations from distilled water were performed on each batch of telluric acid.

The sodium hydroxide solution was standardized with potassium hydrogen phthalate. The borax solution was standardized with standard hydrochloric acid, using methyl red indicator. The arsenious acid solution was standardized with standard iodine, the normality of which had been determined with primary standard arsenious oxide. The telluric acid was standardized by pH titration with the standard base in the presence of propylene glycol.[20] The polyol solutions were prepared by weighing out the polyol, dissolving it in distilled water, and diluting to a known volume.

Procedures. The initial pH data were obtained with the Beckman model G meter, employing glass and calomel electrodes. A reproducibility of $\pm 0{\cdot}02$ pH unit was obtained; this precision is satisfactory for estimation of the larger equilibrium constants. More accurate pH data were obtained

[12] A. DEUTSCH and S. OSOLING *J. Amer. Chem. Soc.* **71,** 1637 (1949).
[13] P. J. ANTIKAINEN *Soumalaisen Tied. Toim. Ann. Acad. Sci. Fennicae* **A56,** (1954).
[14] P. J. ANTIKAINEN *Acta Chem. Scand.* **9,** 1008 (1955).
[15] S. D. ROSS and A. CATOTTI *J. Amer. Chem. Soc.* **71,** 3653 (1949).
[16] F. AUERBACH *Z. anorg. Chem.* **37,** 353 (1903).
[17] B. ENGLUND *Rec. trav. chim.* **51,** 135 (1932); see also
B. ENGLUND *J. Prakt. Chem.* **129,** 1-23 (1931).
[18] A. ROSENHEIM and M. WEINHEBER *Z. anorg. Chem.* **69,** 266 (1911).
[19] F. FOUASSON *Ann. Chem.* **3,** 594 (1948).
[20] J. O. EDWARDS and A. L. LAFERRIERE *Chem.-Anal.* **45,** 12 (1956).
[20a] P. J. ANTIKAINEN *Soumem Kemistilehti B29* **14,** 123, 135 (1956).
[21] F. C. MATHERS, C. M. RICE, H. BRODERICK, and R. FORNEY *Inorganic Syntheses*, Vol. 3, p. 145. L. F. AUDRIETH, Ed. McGraw-Hill, New York (1950).

on the Beckman model GS meter; on its expanded scale it was possible to obtain a reproducibility of $\pm 0{\cdot}003$ pH unit. The expanded scale range was used in all series where the pH depression in the solution with the greatest amount of polyol was less than 3 pH units.

Solutions of arsenious and telluric acids were half-neutralized with sodium hydroxide, thus the concentrations of both the acid (HA) and the anion (A^-) in the buffer stock solution were equal. The chemical constitution of borax is such that its solution is a half-neutralized solution of boric acid just as it is.

Most of the measurements were carried out in the following manner: A fixed amount of buffer stock was placed in each of nine flasks. Then measured amounts of polyol stock and distilled water were added so that the polyol concentration was varied from zero to eight-tenths molar. After the solutions were kept at 25° for at least 20 min, the pH was measured. This procedure was repeated for each buffer with most of the polyols mentioned.[22] The above procedure was modified in the cases of pentaerythritol and polyvinylalcohol, since the former has only limited water solubility and the latter is a polymer without a discrete molecular weight. In addition, the effect of four solvents (dioxane, acetone, ethanol, and methanol) on the pH of the buffer was investigated.

With the tellurate buffers, two general complications which were worthy of note arose. It was found[23] that up to 24 hours were necessary before the complexing equilibrium with certain polyols was established. For this reason, all of the data presented are taken from tellurate systems which were allowed to set at least 1 day before pH measurement. In the borate and arsenite systems, equilibrium appears to be attained in the time of mixing. The other complication lay in the fact that sodium tellurate is fairly insoluble, but does not precipitate rapidly as do most insoluble salts. The rate of precipitation appears to increase as the concentration increases. When the concentration of telluric acid and tellurate ion together was made equal to or less than 0·075 molar, no difficulty was experienced.

RESULTS

General. Some mention of conditions and assumptions is appropriate before the equilibrium constants are discussed. We have assumed throughout that the polyols complex with the anionic forms of the buffers. Such has been the usual conclusion of previous workers, and all of our observations are consistent with this assumption. We have also carried out some polarimetric measurements of the tellurate buffer and mannitol system which again indicated that only the anion form of the buffer is complexed.

The assumption that the values of the complexing constants do not depend on ionic strength seems reasonable, since there is no change in charge type in the reaction. Further, we have kept our salt concentration low (less than 0·1 molar) to avoid specific effects. This argument is not valid for complexes of polyvinyl alcohol, since the complexes are polyelectrolytes.

The methods of calculation depend on the knowledge of the ionization constant of the buffer at the appropriate ionic strength. For each series, the pH of one solution (without polyol) was measured on the pH meter in order to obtain the value of *pKa* to be used in the calculations for all of the other solutions. As the addition of polyol reduces the dielectric constant of the solution slightly, a medium effect on the ionization constant of the buffer is to be expected along with the complexing effect. Additions of small amounts of dioxane, acetone, ethanol, and methanol to each buffer system were carried out in order to estimate the size of the medium effect. The results for tellurate buffer are presented in Fig. 1, which is a plot of the change in pH against the amount of added solvent. It is seen that three of the four solvents cause a small increase in pH, but that methanol does not within the experimental

[22] Under the conditions of our measurements, 3-chloro-1, 2-propanediol and diethyl-D-tartrate were found to hydrolyse; thus, the results with these two polyols are unreliable and have not been presented.
[23] See also discussion in reference 20.

error. The influence of ethylene glycol on the pH of the tellurate buffer is presented for contrast. Similar results were obtained with the arsenite and borate buffers. It is concluded that the medium effect is not large enough to seriously alter the values of the complexing constants for the borate and tellurate systems. The low values found with some arsenite complexes might be slightly larger if the method for correction (see Appendix) is not completely successful.

Except for borate ion, for which there is ample evidence for a second complex containing two polyol molecules, the assumption was made that only a one-to-one complex is present. Most of the data obtained here are in excellent agreement with

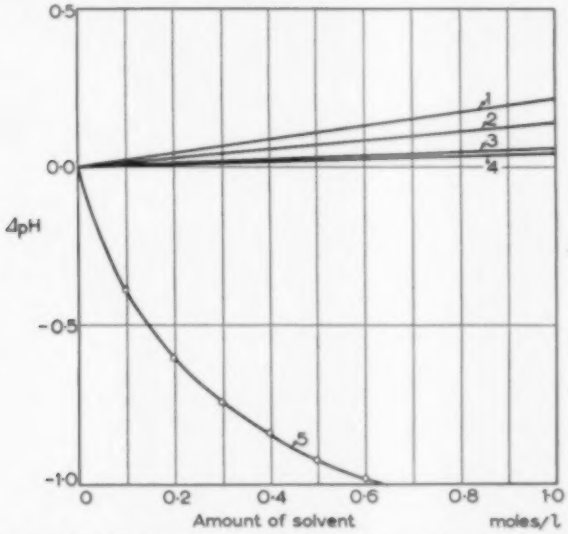

FIG. 1.—Plots showing how five organic liquids influence the pH of the tellurate buffer system: 1, dioxane; 2, acetone; 3, ethanol; 4, methanol; and 5, ethylene glycol.

the predictions of this assumption; in a few cases, however, an unexpected complication arose. The pH changes observed for tellurate buffer solutions with small amounts of mannitol (or sorbitol) could only be explained by calculations based on the assumption that two tellurate ions can be tied up by one mannitol molecule. As both of these polyols have six hydroxyl groups, it is certainly possible for more tellurate ions to be complexed than the number of polyol molecules added. A further complication with the hexahydroxyhexanes is that there are many possible configurations for a one-to-one complex. With these facts in mind, a re-examination of the borate-mannitol system would be worthwhile. Careful studies of other polyols with more than three hydroxyl groups (such as pentaerythritol or galactose) might reveal similar complexes containing two anions per polyol. Only with mannitol and sorbitol were the complications severe enough to prevent the evaluation of complexity constants.

In studies of the present type, one makes the assumption that no chemical reaction other than complexing is occurring. In one case during this study, this assumption was not valid; catechol is slowly oxidized by hexavalent tellurium. All of the tellurate-catechol mixtures became yellow within a few minutes after mixing and

slowly darkened; after several hours, they were brown in colour. A series of solutions left overnight in accordance with our usual procedure was found to contain elemental tellurium. On the sides of some of the flasks, a fine metallic mirror had formed.

Complexing constants. The results of one series of experiments and also the related calculations are presented in Table 1.[24] This tabie, which contains

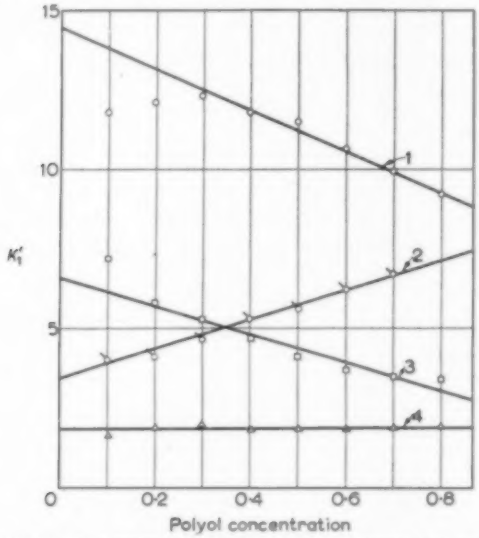

Fig. 2.—Results for four series of experiments: 1, tellurate ion and 2,3-butanediol; 2, borate ion and 2,3-butanediol; 3, arsenite ion and 3-methoxypropylene glycol (times 10); 4, borate ion and ethylene glycol (see Table 1).

data for the mixtures of borate ion and ethylene glycol, shows the steps employed in evaluating K_1' for each point. The values of K_1' can be treated graphically to evaluate K_1, which is defined:

$$K_1 = \frac{[AP^-]}{[A^-][P]}$$

and K_2, which is defined:

$$K_2 = \frac{[AP_2^-]}{[A^-][P]^2}$$

In Fig. 2, the results of the series of Table 1 are presented along with those of three other series; it may be noted that the results are sufficiently precise to allow a satisfactory evaluation of both the slope and intercept. For most of the values of formation constants, it is believed that these are reproducible to $\pm 10\%$. Final values for complexing constants are presented in Table 2. It is worthy of note that the values run from 0·07 to 95,000. At least with the simple polyols, tellurate ion forms the most stable complexes and arsenite ion the least stable complexes.

[24] In this article, the following symbols will be employed: A^- is the anion form of the buffer, HA is the acid form, P is any polyol, AP^- is a one-to-one anion-polyol complex, AP_2^- is a two-to-one complex, K_1' is the formation constant for a one-to-one complex, K_2 is the formation constant for the two-to-one complex. K_1' is a pseudo formation constant (see Appendix), and brackets denote concentration.

TABLE 1.—DATA FOR CALCULATION OF COMPLEXING CONSTANTS
Example—Borate ion and ethylene glycol system

[P]	pH	log [A⁻]	[A]	[AP⁻]	[P]	K_1
0·0	9·186	−1·397	0·04009	—	—	—
0·1	9·124	−1·459	0·03475	0·00533	0·09467	1·62
0·2	9·054	−1·529	0·02958	0·01050	0·18950	1·87
0·3	8·990	−1·593	0·02553	0·01455	0·28545	1·99
0·4	8·956	−1·627	0·02360	0·01648	0·38352	1·82
0·5	8·908	−1·675	0·02113	0·01895	0·48105	1·86
0·6	8·871	−1·712	0·01941	0·02067	0·57933	1·83
0·7	8·827	−1·756	0·01754	0·02254	0·67746	1·89
0·8	8·787	−1·796	0·01600	0·02408	0·77592	1·93

Using a different method based on anion exchange, SARGENT and RIEMAN[25] recently evaluated complexing constants for borate ion and several glycols. Their values for the constants with ethylene glycol, propylene glycol, and glycerol are 1·30, 2·12, and 14·8, respectively.

In Fig. 3, the values of K_1 for the 1,2-polyols are plotted in accordance with the method of linear free energy relationships. As may be seen, the values for borate and arsenite ions correlate well, but those for tellurate ion show little indication of correlation.

Several experiments were performed with arsenate and various polyols. No evidence was found for any complexing of $H_2AsO_4^-$ and the polyols.

TABLE 2.—FORMATION CONSTANTS FOR COMPLEXES OF ANIONS AND POLYOLS

Polyol	Borate		Arsenite	Tellurate
	K_1	K_2	K_1	K_1
Ethylene glycol	1·85	0·1	0·07	16·0
Propylene glycol	3·10	1·60	0·10	30·0
2,3-butanediol [a]	3·45	4·85	0·13	14·5
Phenyl-1, 2-ethanediol	7·45	7·16	0·23	45·6
3-methoxy-1, 2-propanediol	18·8	13·4	0·66	25·0
Glycerol	16·0	41·2	1·15	73·0
D-mannose	50	490	2·30	—
D-glucose	80	770	1·45	14·6
L-(+)-arabinose	130	675	1·60	—
D-(+)-galactose	127	298	1·95	39·2
Fructose	—	95,000	5·50	27·8
Catechol	7,800	14,200	110	—
Polyvinyl alcohol [b]	1·80	4·3	0·70	1·00
Pentaerythritol	240	1,110	1·00	—

[a] Probably a mixture of *d*, *l*, and meso forms.
[b] Constants for polyvinyl alcohol complexes are calculated on the basis of moles of monomeric units per litre.

[25] R. SARGENT and W. RIEMAN *J. Phys. Chem.* **60**, 1370 (1956).

Discussion. Certain results of this study are worthy of further discussion. It is somewhat surprising to note and difficult to explain that any substitution, either electron withdrawing or releasing, on ethylene glycol increases the value of K_1 for complexes of borate and arsenite ion.

The fact that the log values of formation constants for arsenite and borate complexes form a good straight line on the linear free energy plot, indicates that the two anions have similar steric properties. The slope of this line is 0·88. As the borate ion is known to be tetrahedral,[26] one might suspect the arsenite ion to be

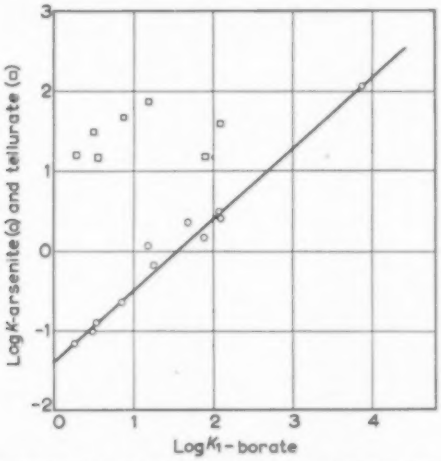

Fig. 3.—Linear free energy plot of equilibrium constants for tellurate complexes (□) and arsenite complexes (○) against those for borate complexes.

$As(OH)_4^-$ and have a distorted tetrahedral structure. No evidence was found for a two-to-one equilibrium, however, so the evidence is not conclusive in favour of the above arsenite structure and the alternative form $AsO(OH)_2^-$ cannot be excluded.

The fact that the K_1 values for tellurate complexes do not correlate with those of arsenite and borate complexes can readily be explained by an unexpected steric requirement of the octahedral structure. Using Fisher-Hirschfelder-Taylor models, it was found that any two *cis* hydroxyl groups on a tellurate ion can easily form complex ions with ethylene glycol by loss of two molecules of water. As groups (such as phenyl or hydroxymethyl) were added to the ethylene glycol, it was found that considerable vibrational and rotational freedom was lost because of the close proximity of the two hydroxyls on telluric acid which are above and below the plane of the five-membered chelate ring. Such loss of freedom of motion in the carbon chain would result in a decrease in the entropy of the complex and thereby lower the value of complexing constant relative to its expected value. With sugar molecules, there was very serious restriction of freedom, but it was still found possible to form a model of the complex. In this model, one of the out-of-plane hydroxyl groups was found to touch the atoms on the pyranose ring of the sugar.

When polyol-borate models were constructed, very little evidence for steric hindrance could be found. It thus seems quite reasonable to attribute the lack of

[26] J. O. Edwards, G. C. Morrison, V. F. Ross, and J. W. Schultz *J. Amer. Chem. Soc.* **77**, 266 (1955).

correlation of formation constants to the different steric requirements of the octahedral anion and the tetrahedral anion.

The complexes of tellurate ion and the polyols were found to have a proton ionization in the same general pH range as the second ionization of telluric acid itself. Our values are not sufficiently accurate, however, to warrant publication at this time.

APPENDIX

Treatment of the experimental data

General. Assuming that only a one-to-one complex is present, it is possible to calculate an equilibrium constant from each pH measurement. In each series, one of these constants must, of course, be for the ionization of the buffer acid. The ionization equilibrium is governed by the mass action expression

$$K_a = \frac{[H^+][A^-]}{[HA]} \tag{I}$$

The complex reaction

$$A^- + P \rightleftharpoons AP^-$$

is governed by the expression

$$K_1 = \frac{[AP^-]}{[A^-][P]} \tag{II}$$

Employing the subscript zero to denote the initial state (before complex formation), the following equations for conservation of mass are valid:

$$[A^-]_0 = [HA]_0 = [HA] \tag{III}$$

and

$$[A^-]_0 = [A^-] + [AP^-] \tag{IV}$$

and

$$[P]_0 = [P] + [AP^-] \tag{V}$$

In every series, one experiment was carried out without polyol in order to evaluate K_a for the whole series. For the balance of the solutions, the three initial concentrations ($[HA]_0$, $[A^-]_0$, and $[P]_0$) and the appropriate value of K_a are known; thus from the measured value of pH of each solution, it is possible, using equations (I), (IV), and (V), to calculate the concentrations to substitute into equation (II) and evaluate K_1.

In practice we prefer to label this calculated value as K_1', since the assumption of a one-to-one complex is not always true, and since medium effects have not been corrected for. In such cases, the equilibrium constant expression for K_1' can be considered to be formulated as

$$K_1' = \frac{[\Sigma AP_n^-]}{[A^-][P]}$$

where $[\Sigma AP_n^-]$ represents the total amount of complexed anion. By substitution of equations (III) and (IV) into equation (VI), one obtains

$$K_1' = \left\{\frac{[HA]_0 - [A^-]}{[A^-]}\right\}\left\{\frac{1}{[P]}\right\}$$

which on further substitution with equation (I) gives

$$K_1' = \left\{\frac{[H^+]}{K_a} - 1\right\}\left\{\frac{1}{[P]}\right\}$$

This use of this equation will be discussed in Case II.

Case I. If only a one-to-one complex were present in solution, it would be expected that the values of K_1' should remain essentially constant as the amount of polyol is varied. A slight downward trend in the values as the amount of polyol increases could be ascribed to the solvent effect on the

value of K_a. Such a solvent effect can be eliminated by plotting the values of K_1' against $[P]$ and extrapolating the nearly horizontal line back to zero $[P]$. Several examples may be seen in Fig. 2.

Case II—With the borate system, it was found that the values of K_1' strongly increased as $[P]$ increased. Plots of K_1' against $[P]$ showed positive slopes and intercepts; these data are explainable on the basis of two different borate complexes containing either one or two glycol molecules.

The conservation of mass equation

$$[B(OH)_4^-]_0 = [B(OH)_4^-] + [B(OH)_2P^-] + [BP_2^-]$$

where $B(OH)_2P^-$ and BP_2^- represent one-to-one and one-to-two complexes respectively, is valid for the borate system. By substitution of the two mass action expressions

$$K_1 = \frac{[B(OH)_2P^-]}{[B(OH)_4^-][P]}$$

and

$$K_2 = \frac{[BP_2^-]}{[B(OH)_4^-][P]^2}$$

followed by dividing through by $[B(OH)_4^-]$ we have

$$\frac{[B(OH)_4^-]_0}{[B(OH)_4^-]} = 1 + K_1[P] + K_2[P]^2$$

From the conditions of our experiments, and from the expression for K_a, we can get

$$\frac{[H^+]}{K_a} = 1 + K_1[P] + K_2[P]^2$$

which may be rearranged to give

$$\left(\frac{[H^+]}{K_a} - 1\right)\left(\frac{1}{[P]}\right) = K_1 + K_2[P]$$

In the case where only one complex is formed, the value of $[P]$ can be calculated. In the present case, it must be estimated. The equation

$$[P] = [P]_0 - [B(OH)_2P^-] - 2[BP_2^-]$$

is the correct equation for conservation of mass; the values of $[P]$ we have employed were obtained from the equation

$$[P] = [P]_0 - \{[B(OH)_2P^-] + [BP_2^-]\}$$

since the total quantity in the {} is known but not the value of either of the terms. As the present experiments were designed so that $[P]_0 > [B(OH)_4^-]_0$, the estimated value of $[P]$ is probably a good approximation to the true value.

From a previous section we have the equation

$$K_1' = \left(\frac{[H^+]}{K_a} - 1\right)\left(\frac{1}{[P]}\right)$$

from which we get by substitution

$$K_1' = K_1 + K_2[P]$$

Thus with the borate-polyol systems, the intercept of a plot of K_1' against $[P]$ gives the value of K_1; the slope of this plot gives the value of K_2.

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THE ANODIC BEHAVIOUR OF COPPER IN AQUEOUS SOLUTIONS

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Abstract—The anodic oxidation of copper in a variety of aqueous electrolytes has been investigated. In the presence of agents (e.g. CN^-, Cl^-, $S_2O_3^=$) which form stable complexes with copper(I), the metal enters solution solely in the unipositive state over a wide concentration range of electrolyte. With a nitrate, sulphate, or chlorate as electrolyte, copper enters solution with an apparent valence number considerably greater than 1 at 25°C. However, as the temperature is increased, the apparent valence number of copper decreases in the presence of these anions. With chlorate at 98°C, the valence number of copper falls to 1. All the experimental data can be explained on the hypothesis that the primary electrode reaction consists of the formation of unipositive copper.

RECENT investigations of the anodic behaviour of some of the active metals of groups II and III of the Periodic System have produced strong evidence for the existence of anomalous lower oxidation states of these metals.[1–7] When an active metal (e.g. magnesium or aluminium) is dissolved as a sacrificial anode in an electrolytic solution containing some easily reducible substance, considerably more metal is dissolved than can be accounted for on the basis of Faraday's law, if it is assumed that the metal of group II or III dissolves wholly as its familiar dipositive or tripositive ion, respectively. This behaviour has been interpreted in terms of the hypothesis that each of the metals is oxidized anodically to a mixture of unipositive ion and the common higher valent ion.

The present paper reports an extensive investigation of the anodic oxidation of copper in aqueous solutions. Copper offers several advantages for an investigation of this type. Ions containing unipositive copper are of course well known and form relatively stable compounds. Thus it seemed probable that the investigation of the anodic behaviour of this metal, both of whose oxidation states are well known, would be helpful toward the understanding of the processes involved in the cases where the lower oxidation state is of low stability. Some differences in behaviour would also be expected, however, because univalent copper is not nearly so strong a reducing agent as the lower valent ions of the more active metals previously investigated.

The anodic behaviour of copper with respect to the valence of the ions entering solution has received relatively little study. SHUKOV[8] found that from a copper anode in an electrolyte capable of complexing with ionic copper, the metal always went into solution with the valence that it normally has in the complex, and that when no complex species was formed, copper(II) only was found in solution. DUSHMAN[9]

[1] A. W. DAVIDSON and F. JIRIK *J. Amer. Chem. Soc.* **72**, 1700 (1950).
[2] W. E. BENNETT, A. W. DAVIDSON, and J. KLEINBERG *ibid.* **74**, 732 (1952).
[3] A. D. MCELROY, J. KLEINBERG, and A. W. DAVIDSON *ibid.* **74**, 736 (1952).
[4] R. L. PETTY, A. W. DAVIDSON, and J. KLEINBERG *ibid.* **76**, 363 (1954).
[5] B. D. LAUGHLIN, J. KLEINBERG, and A. W. DAVIDSON *ibid.* **78**, 559 (1956).
[6] E. RAIJOLA and A. W. DAVIDSON *ibid.* **78**, 556 (1956).
[7] M. D. RAUSCH, W. E. MCEWEN, and J. KLEINBERG *ibid.* **76**, 3622 (1954).
[8] I. SHUKOV *J. Russ. Chem. Soc.* **38**, 1253 (1909).
[9] S. DUSHMAN *J. Phys. Chem.* **14**, 885 (1910).

investigated the dissolution of a copper anode in hydrochloric-acid solution, and devised a treatment by means of which he could calculate a theoretical weight-loss of the anode from the experimental conditions.

Neither the hypothesis that the metal dissolves as a mixture of copper(I) and copper(II) nor the theoretical treatment of DUSHMAN'S appears to be entirely satisfactory for the explanation of all of the experimental data reported in this paper. Therefore, an alternative hypothesis which seems to account satisfactorily for all of the experimental data will be presented: namely, that the metal is initially oxidized solely to the unipositive state, the final result depending upon what then happens to the unipositive ion.

APPARATUS AND EXPERIMENTAL PROCEDURE

The electrolyses were carried out under an atmosphere of oxygen-free nitrogen gas in a cell in which the anode and cathode compartments were separated by a sintered glass disk, as described by DAVIDSON and JIRIK.[1] The current was supplied by a variable voltage full-wave rectifier capable of yielding up to 0·2 A at from 0 to 200 V. During some of the runs the rectifier was modified so as to give only half-wave rectification, in order to test the possibility that some of the loss in weight of the anode might be due to some sort of anodic activation; that is, to nonelectrolytic dissolution of the metal while it is acting as the anode. Each of the electrolyses was carried out for 20 min in a constant-temperature bath with a temperature control of ±0·5°C.

The quantity of electricity passed through the cell during a run was measured by means of a silver coulometer placed in series with the electrolytic cell. The current was held constant at the desired value by manual variation of the applied cell voltage. The current densities are reported as amp per square centimetre of apparent anode area, no attempt having been made to determine the true anode area.

The electrodes were cut from a 4-mm-diameter wire of electrolytic grade copper, at least 99·9% pure. The anode and cathode of the cell were identical in all respects. All chemicals used were of reagent grade.

The anode was cleaned in dilute hydrochloric acid, washed with distilled water, dried, and weighed before and after each run. A copper rod having approximately the same exposed surface area as the anode, and subjected to the same cleaning procedure, was placed in the anolyte below the anode during the electrolysis. The loss in weight of this control was subtracted as a "blank" from the loss in weight of the anode in order to correct for nonelectrolytic corrosion. This correction will be further referred to only in those cases in which it is large enough to be significant.

The results have been expressed in terms of the initial mean valence number, V_i, of the copper cation produced. This number, calculated by means of the equation

$$V_i = \frac{\text{wt. of Ag deposited in the coulometer} \times 63{\cdot}54}{107{\cdot}88 \times \text{wt. of Cu lost from the anode}}$$

corresponds, of course, to the average number of electrons lost by a copper atom as it goes into solution. Each result reported is the average of at least two determinations under the same conditions. When two such determinations differed by more than $0{\cdot}05V_i$ unit, the reported result is the average of at least three determinations.

ELECTROLYSES AT CONSTANT CURRENT DENSITY AND TEMPERATURE

The V_i of a copper anode was determined at varying electrolyte concentration in solutions of several different electrolytes at a constant temperature and current density.

Sodium chloride

Electrolyses were carried out in a number of different sodium chloride solutions, varying in concentration from saturation (about 10 mole per cent) to 0·07 mole per cent. At concentrations

greater than 5 mole per cent, the V_t value was found to be 1·00 ± 0·01. The results at concentrations less than 5 mole per cent are presented graphically in Fig. 1.

In two determinations, one at 3·00 and one at 0·46 mole per cent, in which intermittent direct current was used, no change in V_t was observed.

At concentrations more dilute than 1·40 mole per cent, the anode became coated with an adherent coating of copper(I) chloride. This concentration corresponds to the sharp break in the V_t vs. sodium chloride concentration curve of Fig. 1.

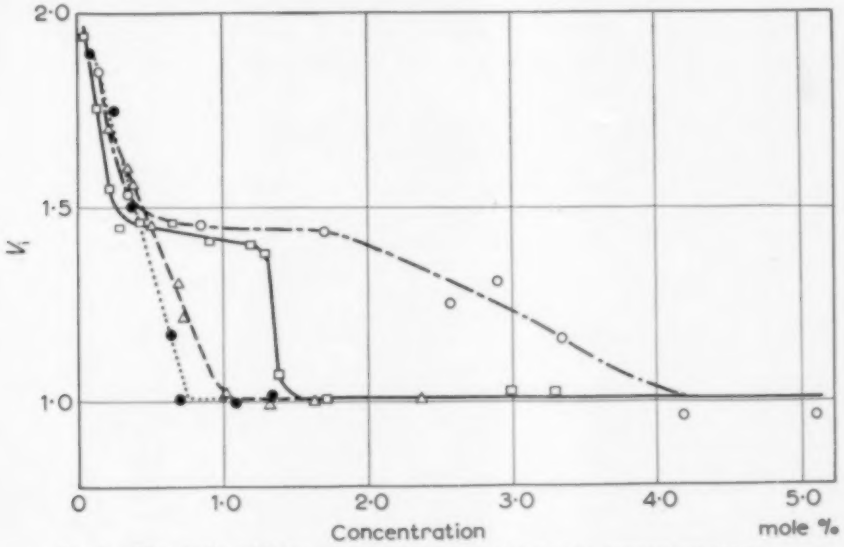

FIG. 1.—The anodic oxidation of copper in various electrolytes; temperature 40°C; current density 0·015 amp/sq. cm.

□ ——— sodium chloride. △ — — — sodium thiosulphate (25°).
○ — · — sodium bromide. ● ····· sodium cyanide + sodium sulphate.

The rather unexpected shape of this curve calls for an adequate explanation. At concentrations greater than about 1·5 mole per cent the overall electrode reaction appears to consist of the formation of a copper(I) chloride complex ion:

$$Cu + nCl^- \rightarrow CuCl_n^{1-n} + e^- \qquad (1)$$

It seems probable that this equation expresses the net result of the consecutive reactions

$$Cu \rightarrow Cu^+ + e^- \qquad (2)$$

$$Cu^+ + nCl^- \rightarrow CuCl_n^{1-n} \qquad (3)$$

Reaction (2) is presumably the primary electrode reaction, and reaction (3) then takes place in the solution near the anode surface. Thus a steady-state condition exists in the neighbourhood of the anode, reaction (3) removing the uncomplexed copper(I) ion from solution as fast as it is formed by reaction (2).

It should, perhaps, be pointed out that the production of the simple copper(I) ion may not be as direct as is indicated by reaction (2). The copper(I) ion may be formed by means of a secondary attack on the anode by the anion, as postulated by

AUDUBERT.[10] Since the important point here is the formation of copper(I) ion, equation (2) as written will be used to represent this reaction.

The approach to constancy of the values obtained for V_i in the concentration range from 0·3 to 1·3 mole per cent, and their approximation to the figure 1·5, strongly suggest that a complex species containing both copper(I) and copper(II), in equimolar proportions, is formed in this range. There is, indeed, some independent evidence for the existence of such a complex species. It is well known that when copper(I) and copper(II) salts are present together in concentrated hydrochloric-acid solution, an intense brown colour results. KOHLSCHÜTTER[11] and PARTINGTON and SKEEN[12] observed the same colour in nonaqueous solutions, and obtained electrochemical evidence that the complex species formed contains equimolar amounts of copper(I) and copper(II).

One possible series of reactions which would account for the behaviour of the system in this concentration range is the following:

$$Cu \rightarrow Cu^{+} + e^{-} \tag{2}$$

$$Cu^{+} + Cl^{-} \rightarrow CuCl \tag{4}$$

Part of the copper(I) chloride is then oxidized at the anode:

$$CuCl \rightarrow Cu^{++} + Cl^{-} + e^{-} \tag{5}$$

The copper(II) formed then reacts with the remaining copper(I) chloride and additional chloride ion to give the copper(I)-copper(II) complex:

$$CuCl + Cu^{++} + (n-1)Cl^{-} \rightarrow Cu_2Cl_n^{3-n} \tag{6}$$

The complex species diffuses out into the body of the solution, where at a lower chloride-ion concentration it decomposes into copper(I) chloride, copper(II) ion, and chloride ion; this hypothesis would account for the fact that no brown colour was observed in the solution.

The second sharp increase of V_i with decreasing concentration, at concentrations of less than 0·3 mole per cent sodium chloride, can also be readily explained in terms of the foregoing reactions. The decrease in chloride-ion concentration in the neighbourhood of the anode decreases the rate of reaction (6) until more than half of the copper(I) chloride produced by reaction (4) is being oxidized according to reaction (5); thereafter, the V_i value must rise toward a maximum of 2.

The number of chloride ions associated with each copper(I) ion in the complex species, under experimental conditions such that the V_i was 1·00, was determined by the potentiometric method of SZABO.[13] The complex species was found to be $CuCl_3^{-}$, which formula confirms the results obtained by SZABO under considerably different experimental conditions and concentrations.

Sodium bromide

The V_i values were determined for concentrations of sodium bromide from 5·06 to 0·17 mole per cent, with the results shown in Fig. 1.

In the concentration region above about 2·0 mole per cent, two determinations of V_i at the same concentration often varied by as much as 0·15 V_i unit. Considerable difficulty was encountered also,

[10] R. AUDUBERT *Compt. rend.* **239**, 1792 (1954).
[11] V. KOHLSCHÜTTER *Ber.* **37**, 1153 (1904).
[12] J. R. PARTINGTON and J. W. S. SKEEN *Trans. Faraday Soc.* **32**, 975 (1936).
[13] Z. SZABO *Magyar Chemiai Folyoirat* **39**, 1 (1933).

at these concentrations, in the maintenance of a constant current. Even in this region, however, the general nature of the anodic behaviour was clear enough. At concentrations lower than 2·0 mole per cent no difficulties were encountered and the behaviour was much more reproducible.

Since the general similarity of the two curves is apparent, it would seem that an interpretation analogous to that given for the chloride electrolyte would apply equally well here. The difference in shape of the two curves is understandable if the copper(I) halide and particularly the halide complex species containing both copper(I) and copper(II) are less stable in bromide than in chloride solutions.

Sodium thiosulphate

V_i values determined for concentrations ranging from 2·49 to 0·22 mole per cent of sodium thiosulphate, at a temperature of 25°C, are given in Fig. 1. Because of the difference in temperature, the results of this series are not strictly comparable with the rest of the results shown in Fig. 1. However, a 15° temperature increase would not be expected to change the general shape of the thiosulphate curve; the probable effect would be to shift the position of the curve slightly to the right.

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The general shape of this curve may be explained in terms of the following mechanisms. At thiosulphate concentrations greater than 1·0 mole per cent, the principal product is a copper(I) thiosulphate complex ion formed by means of the reactions

$$Cu \rightarrow Cu^{+} + e^{-} \tag{2}$$

$$Cu^{+} + nS_2O_3^{=} \rightarrow Cu(S_2O_3)_n^{1-2n} \tag{7}$$

According to SIDGWICK,[14] the complex ion formed between copper(I) and thiosulphate ion is probably $CuS_2O_3^{-}$; i.e. $n = 1$. In solutions of thiosulphate concentration less than 1·0 mole per cent, the rate of reaction (7) is reduced to such an extent that the anode reaction

$$Cu^{+} \rightarrow Cu^{++} + e^{-} \tag{8}$$

begins successfully to compete with reaction (7) for the removal of the unstable uncomplexed copper(I) ion. Such competition might well give rise to the smooth increase of V_i which is experimentally observed.

Sodium cyanide

With sodium cyanide concentrations of less than 0·73 mole per cent, gas was evolved at the anode and the calculated V_i values were greater than 2, indicating that some electrode process other than the dissolution of copper must be taking place. In the concentration range between 0·73 and 1·80 mole per cent sodium cyanide, V_i was found to be 1·00 ± 0·02. In solutions more concentrated than 1·8 mole per cent, the nonelectrolytic corrosion of metallic copper by the cyanide ion became a significant factor and the V_i values fell below 1.

Sodium sulphate

In sodium sulphate solutions ranging in concentration from 3·64 to 0·12 mole per cent, the results, apparently independent of concentration, varied more widely among solutions of identical composition than in any previous case. The nonelectrolytic corrosion, as indicated by the loss in weight of the blank, was large enough—about 0·05 V_i unit—so that it had to be taken into consideration. The corrected V_i value obtained under these conditions was 1·96 ± 0·08. The lack of precision in this series of measurements is difficult to explain. Apparently this system is very sensitive to small changes in some variable other than the closely controlled temperature and electrolyte concentration.

[14] N. V. SIDGWICK *The Chemical Elements and Their Compounds* Vol. 1, p. 145. Oxford University Press, London (1950).

Sodium nitrate

V_i values were determined in solutions containing from 4·0 to 1·0 mole per cent sodium nitrate. Here again the results seemed to be essentially independent of concentration. The correction for nonelectrolytic corrosion was found to be about 0·05 V_i unit, and the corrected V_i value was found to be 1·98 ± 0·04.

Sodium iodide, sodium fluoride, and sodium thiocyanate

When sodium iodide was used as electrolyte, white insoluble copper(I) iodide was produced as a rather loose coating on the anode, and as soon as this coating became fairly thick, free iodine began to be formed at the anode. However, when a concentrated iodide solution was used, the appearance of free iodine could be delayed long enough for a V_i determination to be made. By this means, V_i values as low as 1·05 were obtained.

Surprisingly, it was found that a sodium fluoride solution slowly attacked metallic copper non-electrolytically under the conditions of electrolysis. The correction for nonelectrolytic corrosion was too large to be considered accurate, and about all that can be stated with certainty is that the corrected V_i was larger than 1·9.

In sodium thiocyanate solutions, a copper anode was found to be completely passive.

Mixed sodium chloride–sodium sulphate solutions

The extent to which the lowering of V_i below 2 that occurs in chloride media persists in a mixture of chloride and some anion, such as sulphate, that does not itself cause significant lowering, was next investigated. The overall electrolyte concentration was held constant at 2·0 mole per cent, and the relative amounts of sulphate and chloride ions were varied.

A comparison of the values obtained for the mixed electrolyte with those obtained for sodium chloride alone, shows that the V_i values were the same, to within 0·04 V_i unit, as in pure sodium chloride solution of the same chloride-ion concentration. Thus it would appear that the extent of V_i lowering is dependent upon the chloride-ion concentration only.

Mixed sodium cyanide–sodium sulphate solutions

The overall electrolyte concentration was held at 1·36 mole per cent and the relative amounts of cyanide and sulphate were varied.

The results are given in Fig. 1, where V_i is plotted against cyanide-ion concentration. From a comparison of these results with those obtained for the mixed chloride-sulphate electrolyte, it would seem that the behaviour of this system might be considered as that which a copper anode would exhibit in a pure sodium cyanide solution if it did not become passive.

The shape of the curve obtained here is very similar to that found for sodium thiosulphate solutions, and a similar interpretation may be given.

When the cyanide-ion concentration was between 0·63 and 0·27 mole per cent, a bright green crystalline solid was formed at the anode. After having been washed with distilled water and allowed to air-dry for several days, the green substance gave the following analysis; Cu 46·9%, CN 30·0%, H_2O 23·1%. The analysis corresponds well with the empirical formula $Cu_3(CN)_4 \cdot 5H_2O$. A compound of the same properties and composition, which is better formulated as $Cu^{II}[Cu^{I}(CN)_2]_2 \cdot 5H_2O$, has been previously prepared by the spontaneous decomposition of freshly precipitated copper(II) cyanide.[15]

[15] H. E. WILLIAMS *Cyanogen Compounds*, p. 112. Edward Arnold and Co., 2nd ed. London (1948).

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EFFECT OF VARIATION OF CURRENT DENSITY ON V_i

Sodium chloride solutions

Three series of determinations were carried out, with sodium chloride as electrolyte, at current densities of 0·067, 0·014, and 0·0027 amp/sq. cm. This was about as large a variation as could be conveniently made without modification of the apparatus. The results of these series are given in Fig. 2.

Considerable difficulty was encountered in obtaining satisfactory results at a current density of 0·067 amp/sq. cm and concentrations less than about 4 mole per cent. The current tended to oscillate widely, with a period of several seconds. Such periodic variation in behaviour of a copper anode in sodium chloride solutions at certain concentrations and current densities has been studied previously.[16] The oscillations were corrected for, as far as possible, by manual variation of the applied cell voltage. The values of V_i obtained varied widely from run to run, the difference between two determinations under the same conditions being as much as 0·2 V_i unit. Thus the V_i values reported for this range must be considered to be only approximate. Under all other conditions the results were reproducible to 0·03 V_i unit or better.

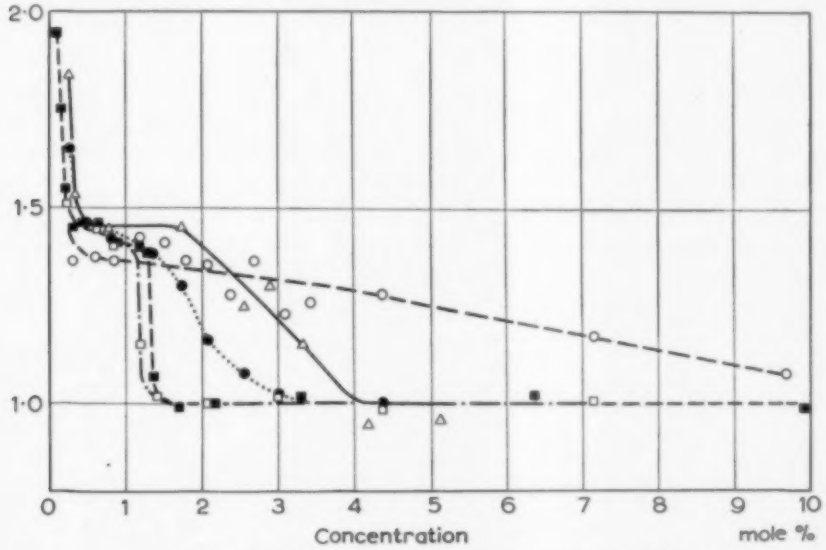

FIG. 2.—Effect of current density on V_i; temperature 25°C.
○ — — sodium chloride, 0·067 amp/sq. cm. △ —— sodium bromide, 0·014 amp/sq. cm.
■ - - - - - sodium chloride, 0·014 amp/sq. cm. ● . . . . . sodium bromide, 0·0027 amp/sq. cm.
□ — · — sodium chloride, 0·0027 amp/sq. cm.

The results at 0·0027 and 0·014 amp/sq. cm are seen to be very similar, the only difference being that the sharp rise in V_i which accompanies the appearance of solid copper(I) chloride on the anode, as would be expected, occurs at a somewhat lower concentration with the lower current density. The mechanism previously proposed for the rise in V_i seems to be applicable here also.

At a current density of 0·067 amp/sq. cm, a V_i of 1 is never obtained even in the most concentrated solutions. The erratic results at this higher current density—and consequently higher anode potential—perhaps may be best explained in terms of the hypothesis that the primary electrode reaction

$$Cu \rightarrow Cu^+ + e^- \qquad (2)$$

[16] K. F. BONHOEFFER and H. GERISHER *Z. Elektrochem* **52**, 149 (1948).

is followed by a number of the following reactions occurring simultaneously: (3), (4), (5), and (8).

The results obtained in this investigation do not confirm the observations of SHUKOV,[8] who reported that a low current density favoured the formation of copper(II).

Sodium bromide solutions

The shape of the curve obtained when V_t vs. concentration was plotted for sodium bromide solutions electrolysed at a current density of 0·014 amp/sq. cm was intermediate between those for sodium chloride solutions at 0·014 and 0·067 amp/sq. cm. Therefore, a series of V_t determinations

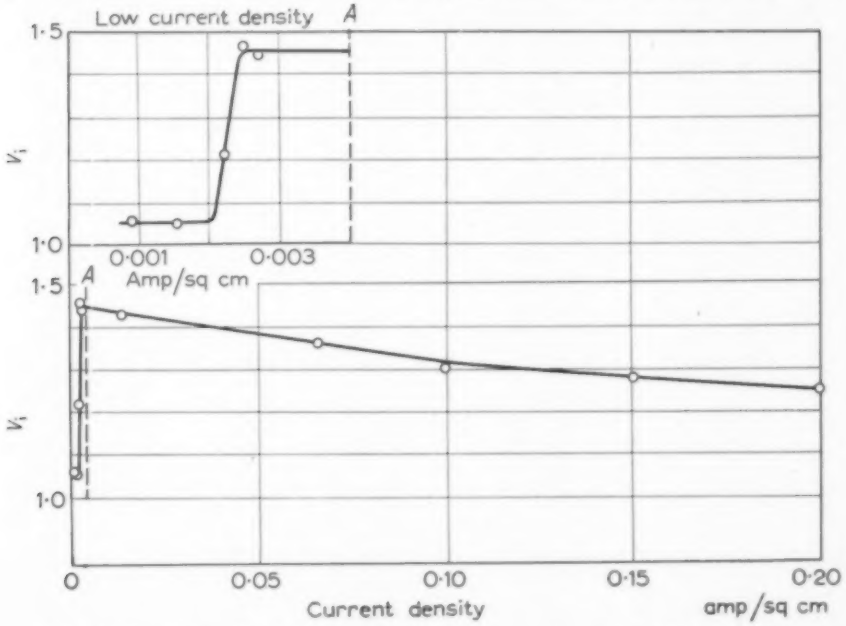

FIG. 3.—Copper anode in sodium chloride solution; concentration 0·91 mole per cent; temperature 25°C.

in sodium bromide solutions at a lower current density was made, in order to see if sharper breaks could be obtained. The results of the two series of V_t determinations in sodium bromide solutions are compared in Fig. 2.

Again the results are about what would be expected from the mechanism previously proposed. The principal difference between the two series is that at the lower current density there is a slightly greater tendency for the copper(I) bromide complex to be formed.

Variation of current density at constant concentration

A series of V_t determinations was carried out at a constant concentration of 0·91 mole per cent sodium chloride and various current densities. The results of this series are shown in Fig. 3.

The sharp break at a current density of 0·0021 amp/sq. cm was accompanied by the appearance of solid copper(I) chloride oo the anode surface, and would seem,

as in the case of similar break in the V_i vs. concentration series, to be due to the change of the secondary reaction from

$$Cu^+ + 3Cl^- \rightarrow CuCl_3^{--} \quad (3)$$

to

$$Cu^+ + Cl^- \rightarrow CuCl \downarrow \quad (4)$$

At current densities of 0·067 amp/sq. cm and higher, the anode compartment was warm to the touch at the end of a run, even though it was immersed in a constant-temperature bath at 25°C. Local boiling was observed at the surface of the anode at a current density of 0·20 amp/sq. cm. Since this observation suggested the possibility of a temperature effect on V_i, a run was made at a current density of 0·067 amp/sq.cm and a temperature of 97°C: here the V_i was found to be 1·04. Thus the gradual decrease in V_i with increasing current density, at current densities greater than 0·003 amp/sq. cm, would seem to be primarily an effect of increasing temperature rather than of increasing current density.

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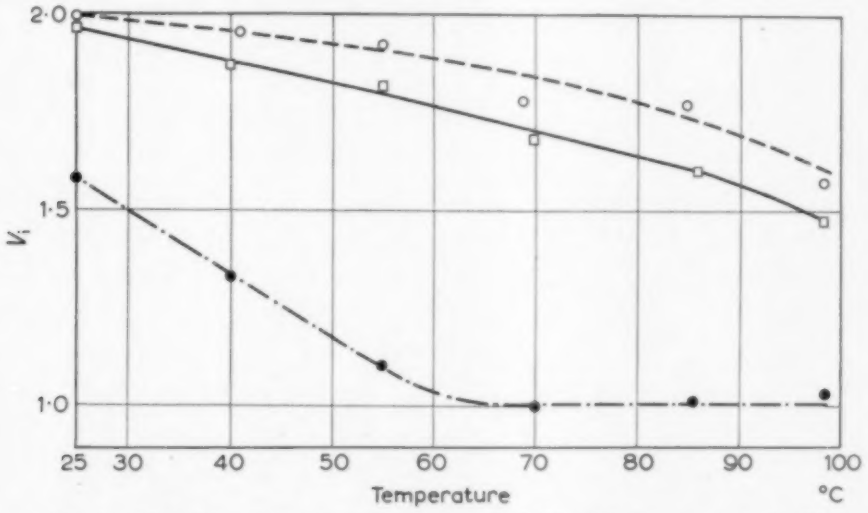

FIG. 4.—Effect of temperature on V_i; current density 0·015 amp/sq. cm; concentration 2·07 mole per cent.
○ — — — sodium nitrate.
□ ——— sodium sulphate.
● — · — sodium chlorate.

EFFECT OF TEMPERATURE ON V_i

The result just described suggested the desirability of a more extensive investigation of the variation of V_i with temperature. The concentration of electrolyte and the current density were held constant, and V_i values were determined at temperatures from 25° to 100°C.

Sodium nitrate

The V_i values found for a copper anode in sodium nitrate solution, at temperatures from 25° to 97°C, are given in Fig. 4. The reported values include a slight correction for nonelectrolytic corrosion. The loss in weight of the copper blank was such that this correction amounted, at all temperatures, to about 0·04 V_i unit. The results were somewhat erratic, two determinations at the

same temperature sometimes varying by as much as 0·10 V_i unit; the reported values are the average of at least three determinations.

The results at temperatures above 25°C show that at least some of the copper must enter the solution as copper(I). In view of the well-known instability of copper(I) ion in aqueous solution in the absence of strong complexing agents, it seemed probable that the low V_i values were due to the immediate oxidation of this species by nitrate ion.

The validity of this hypothesis was demonstrated by the following experiment. The anode compartment of the cell was filled with sodium nitrate solution, and the cathode compartment was filled with sodium sulphate solution of the same concentration to prevent the cathodic formation of reduction products of nitrate ion. After electrolysis, samples of the original nitrate solution, the catholyte, and the anolyte were examined for the presence of nitrite ion by means of the diphenylamine test.[17] The anolyte gave a positive test for the presence of nitrite ion, whereas the catholyte and the starting solution gave negative tests. Thus, reduction of nitrate ion must have taken place in the anode compartment. If the nitrite had been formed by direct action of metallic copper, the weight-loss of the blank would have been much larger, and dependent upon temperature.

The behaviour of a copper anode in solutions containing nitrate ion is somewhat different from that of the more active metals magnesium, beryllium, and the aluminium family.[1–5] With these more active metals, oxidation by nitrate ion of the lower valent metal ions formed during the electrolysis is rapid enough even at room temperature to compete successfully with anodic oxidation of these ions. On the other hand, the oxidation of copper(I) by nitrate ion does not proceed at a significant rate until the temperature is raised.

Sodium sulphate

A similar series of V_i determinations was made with a sodium sulphate electrolyte, with results as shown in Fig. 4.

These results were even more erratic than those of the previous series. Two determinations under the same conditions differed by as much as 0·18 V_i unit. Each reported result is the average of at least three determinations at the same conditions. The correction for nonelectrolytic corrosion came to 0·03 V_i unit or less in all cases, and showed no change with temperature.

As in the preceding series, the V_i values obtained show that some of the metal must have entered the solution as copper(I). Hence, the anolyte was examined for the presence of a reduction product of sulphate ion. The fact that the anolyte decolorized acid permanganate solution showed that either copper(I) or a reduction product of sulphate ion was present. The reducing species was identified by the following procedure. Sodium sulphate solution was placed in the anode compartment, and sodium chloride of the same concentration was placed in the cathode compartment to eliminate the possibility of the cathodic reduction of sulphate to a product which might then migrate into the anode compartment. An electrolysis was then carried out in the usual manner at a temperature of 97°C. The stream of nitrogen gas which passed through the anode compartment during the electrolysis was bubbled through an acid permanganate solution. At the end of the electrolysis the anolyte

[17] W. C. OEKLE *Semimicro Qualitative Analysis*, p. 143. D. C. Heath and Co., Boston (1950).

was acidified and about three-fourths of the solution was distilled into the permanganate solution. The excess permanganate was reduced with concentrated hydrochloric acid and barium chloride solution was added. The formation of a white precipitate of barium sulphate demonstrated the presence of sulphur dioxide in the anolyte.

Sodium chlorate

The results of the series with nitrate and sulphate solutions suggested the trial of an anion which is a more rapid oxidizing agent. Hence, a similar series was carried out with sodium chlorate as electrolyte. This salt offers the additional advantage that the chloride ion formed by the reduction of chlorate can be determined quantitatively with relative ease and accuracy. The V_i values obtained in this series also are shown in Fig. 4.

In contrast to the high-temperature runs in sulphate or nitrate solutions, the results in sodium chlorate solutions were highly reproducible and no two determinations at the same temperature differed by more than 0·02 V_i unit. Here again a small correction for nonelectrolytic corrosion had to be made; the largest correction, however, was only 0·03 V_i unit.

Despite the fact that it was labelled as reagent-grade material, the sodium chlorate used gave a faint positive test for chloride ion. Thus it was necessary to determine the quantity of this impurity and to take it into consideration in the calculations. The amount of chloride ion formed in the anode compartment was determined in the following manner. The anode compartment was filled with sodium chlorate solution and the cathode compartment with sodium sulphate solution of the same concentration. An electrolysis was then carried out in a normal manner at 98°C. Under these conditions no chloride ion could be detected in the cathode compartment; the increase in chloride ion in the anolyte was assumed to be due to the reaction

$$6Cu^{+} + ClO_3^{-} + 3H_2O \rightarrow 6Cu^{++} + Cl^{-} + 6OH^{-}$$

At the end of the electrolysis the anode was cleaned with a small amount of dilute nitric acid, which was added to the anolyte. The chloride ion in the anolyte was then determined by means of potentiometric titration with standard silver-nitrate solution.

On the assumption that the V_i of the copper was exactly 1·00, the amount of copper(I) formed was determined from the gain in weight of the silver coulometer, and the amount of chloride which would be produced by the oxidation of this copper(I) to copper(II) was calculated. A comparison of actual chloride found with theoretical chloride is given in Table 1.

Thus the reduction product formed in the anode compartment can be quantitatively correlated with the extent of V_i lowering.

TABLE 1.—CHLORIDE ION FORMED IN SODIUM CHLORATE SOLUTION
(Current density 0·015 amp/sq. cm; concentration 2·07 mole per cent)

Chloride (found) (moles × 10^4)	Chloride (theoretical) (moles × 10^4)	Per cent of theoretical found
2·197	2·242	98·1
1·404	1·387	101·3
2·016	2·056	98·3
		Average 99·3

At temperatures of 70°C and higher a blue-green crystalline solid was formed in the anode compartment. This material was analysed and was found to have the following composition by weight: Cu 54·2; Cl 15·0%. These data agree very well with the empirical formula $Cu_4Cl_2O_3$ (calcd.: Cu 54·2,

Cl 15·1%). A sample of the material gave negative tests for the presence of chloride, hypochlorite, and chlorite ions. This suggests the formulation $Cu(ClO_3)_2 \cdot 3CuO$. Insoluble blue-green basic chlorates of compositions corresponding to the formulas $Cu(ClO_3)_2 \cdot CuO$[18] and $Cu(ClO_3)_2 \cdot 3Cu(OH)_2$[19] (calcd.: Cu 49·8, Cl 13·9%) have been prepared, but apparently the compound $Cu(ClO_3)_2 \cdot 3CuO$ has not been previously reported.

The V_i values obtained in a sodium chlorate solution at temperatures of 70°C and above indicate that under these conditions, at least, practically all of the copper enters the solution as copper(I). An increase in temperature, when the current density, the concentration of electrolyte, and the applied cell voltage all remain virtually constant, would not be expected to bring about a change in the primary electrode reaction. Thus it appears likely that at all temperatures the copper enters solution initially in the unipositive state. At lower temperatures the chlorate ion is not a sufficiently rapid oxidizing agent to convert all of the +1 copper to the dipositive state, and the process

$$Cu^+ \rightarrow Cu^{++} + e^- \qquad (8)$$

takes place to some extent at the electrode. As the temperature is raised, the effectiveness of chlorate as an oxidizing agent increases, and the secondary electrode process becomes less significant. The V_i value obtained is, therefore, an indication of the relative amounts of copper(I) which are being oxidized by the two reactions.

There is no reason to suppose that the processes occurring with sodium nitrate or sodium sulphate solution as electrolyte are essentially different from that which takes place with sodium chlorate. This analogy, of course, is not definitely proven by the experimental evidence. However, when the electrolyte concentration and the current density were kept constant, virtually the same applied cell voltage was required at all temperatures. Hence it would appear reasonable to assume that the initial electrode process is the formation of the copper(I) ion. Again, as in the case of sodium chlorate, the decrease in V_i with increasing temperature is to be accounted for by the plausible hypothesis that the anion, i.e. NO_3^- or $SO_4^=$, is a more effective oxidizing agent at higher temperatures.

CONCLUSIONS

As a result of the experiments both in the presence of complexing and oxidizing anions, the following general conclusion may be reached regarding the anodic oxidation of copper. The primary anode reaction appears to be the formation of copper(I). That V_i values greater than one are often obtained is due to the tendency of the unipositive copper to lose an electron to the anode with the formation of copper(II). However, this second reaction may be inhibited in either of two ways: (a) the copper(I) may be stabilized by complex formation; (b) the copper(I) may be chemically oxidized by some anion such as chlorate or nitrate. The actual V_i value obtained in any particular instance depends upon the relative rates of the electrochemical oxidation on the one hand and the chemical reaction of either type (a) or (b) on the other.

[18] M. C. SNEED, J. L. MAYNARD, and R. C. BRASTED *Comprehensive Inorganic Chemistry* Vol. 2, p. 101. D. Van Nostrand Co. Inc., New York (1954).
[19] A. BUTTS *Copper: the Metal, its Alloys and Compounds* p. 794. Reinhold Publishing Corp., New York (1954).

This proposed mechanism would appear to apply equally well to the anodic oxidation of the more active metals previously investigated,[1–7] the only exception being that no clear-cut example of a chemical reaction of type (a) has been encountered as yet. The behaviour of metals of the aluminium family in a mixed nitrate-halide electrolyte, however, seems to indicate a slight tendency toward a reaction of this type.

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STUDIES IN ALUMINIUM SOAPS—II

MONO- AND DI-SOAPS OF ALUMINIUM

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Abstract—Strong evidence has been adduced for the existence of mono- and di-soaps of aluminium by preparative methods. Mono-and di-isopropoxy laurates and stearates of aluminium have been prepared by metathetic reactions between aluminium isopropoxide and the calculated amount of the corresponding fatty acid. The isopropoxy-laurates, on treatment with acetyl chloride, have been shown to yield mono- and di-chloride laurates. All these soaps give solutions of low viscosity in benzene. When the di-isopropoxy stearate was treated with acetic anhydride, the isopropoxy as well as the stearate groups were replaced by acetoxy radicals and thus no pure acetoxy-soap could be isolated.

THE existence of tri-, di-, and mono-soaps of aluminium has been in question for a long time. Conflicting opinions have been expressed regarding all the three types. The literature regarding tri-soaps has been reviewed in a recent publication.[1] The existence of di- and mono-soaps has also been in doubt. GRAY and ALEXANDER[2] carried out a detailed study of the reactions between aluminium secondary butoxide and different mono-carboxylic acids and came to the conclusion that the mono-soaps did not exist as definite chemical compounds. They also expressed doubts regarding the existence of di-soaps. The preparation and properties of di-soaps have, however, been described by K. J. MYSELS and co-workers in recent publications.[3,4]

In earlier publications,[1,5] it has been shown that aluminium tri-carboxylates of higher fatty acids can be prepared by the following reaction:

$$Al(OPr^i)_3 + 3RCOOH \rightarrow Al(OOCR)_3 + 3Pr^iOH,$$

if the isopropanol produced is continuously fractionated out azeotropically with benzene. After the conclusion of the present investigation, the authors have noticed that the above findings have been confirmed in a recent publication.[6] The present authors have also described the preparation of lower tri-carboxylates of aluminium by the reaction between aluminium alkoxides and the corresponding acid anhydride.[7]

It has been shown in the present investigation that when one mole of aluminium isopropoxide is treated with one mole of the fatty acid, the replacement of the alkoxy group is rapid and the product thus obtained corresponded in analysis to the di-isopropoxy mono-carboxylate. Similarly the reaction of aluminium isopropoxide with two moles of a fatty acid leads to the formation of aluminium mono-isopropoxy di-carboxylate. It has been further demonstrated that the remaining

[1] R. C. MEHROTRA and K. C. PANDE *J. Inorg. Nucl. Chem.* **2**, 60 (1956).
[2] V. R. GRAY and A. E. ALEXANDER *J. Phys. Chem.* **53**, 23 (1949).
[3] G. H. SMITH, H. H. POMEROY, C. G. MCGEE, and K. J. MYSELS *J. Amer. Chem. Soc.* **70**, 1053 (1948).
[4] K. J. MYSELS and D. M. CHIN *J. Amer. Chem. Soc.* **75**, 1750 (1953).
[5] R. C. MEHROTRA *Nature* **172**, 74 (1953).
[6] A. GILMOUR, A. JOBLING, and S. M. NELSON *J. Chem. Soc.* 1972 (1956).
[7] K. C. PANDE and R. C. MEHROTRA *Z. anorg. Chem.* **286**, 291 (1956).

isopropoxy groups in these derivatives can be replaced by the chloride groups when these are treated with acetyl chloride. The mono- and di-chloro soaps of aluminium have been prepared in this manner. It was further attempted to replace the alkoxy group in the iso-propoxy soaps of aluminium with the acetoxy group with a view to prepare the acetoxy-soaps of aluminium. However, when the alkoxy-soaps of aluminium were treated with acetic anhydride in the presence of benzene, the alkoxy as well as some of the fatty acid groups were found to be attacked; thus no pure derivatives could be isolated by this reaction.

The isopropoxy- and chloride-soaps of aluminium were found to be soluble in benzene giving solutions of low viscosity. These observations are in conformity with that of MYSELS and CHIN,[4] who found that the monochloro dilaurate of aluminium is a nonthickener for hydrocarbons and differs in this respect from the hydroxy derivatives.

EXPERIMENTAL

Apparatus and materials

The experimental technique followed was similar to that already described.[1] Aluminium isopropoxide, benzene and fatty acids were purified as before. Acetic anhydride and acetyl chloride (E. Merck products) were carefully fractionated over a column before use and were directly distilled into the reaction mixture. At every stage, special precautions were taken to exclude moisture completely.

Analytical methods

Aluminium was determined as oxide by the direct ignition of the alkoxy and acetoxy soaps. In the case of chloride-soaps the ignition was done in presence of ammonium carbonate. The alkoxy contents were determined by oxidation with chromic acid as already described[5] and it was confirmed that the fatty acid contents of the mixed soap did not affect the chromic acid. Chlorine was estimated by PIRIA and SCHIFFS' method. The isopropanol in the benzene-isopropanol azeotrope was also estimated by the oxidimetric method already described.

General procedure

The method of fatty acid interchange employed was similar in all cases, and therefore for brevity details are given only for the preparation of aluminium di-isopropoxy monolaurate.

Dry benzene (80 c.c.) was distilled into a mixture of aluminium isopropoxide (5·9 g) and lauric acid (5·88 g) (molar ratio of isopropoxide to acid = 1 : 1). The mixture was refluxed at a bath temperature of 120°. About 5 c.c. of the distillate was collected at 71° within a short time (about 15 minutes), when the temperature of the distilling liquid started rising. It was allowed to reflux for another half an hour and then another fraction (10 c.c.) of the distillate was collected between 71°–80° slowly, within half an hour. These two fractions were found to contain 1·6 g of isopropanol against 1·7 g needed for the replacement of one mole of the isopropoxy group. At this stage the temperature of the distilling liquid became steady at 80°. Pure benzene was, therefore, distilled under a high reflux ratio (1 : 20). The product was present in the form of a mobile solution in the remaining benzene. This benzene was removed by distillation under reduced pressure (4 mm) by heating in a bath at 40° for nearly one hour. A colourless viscous liquid (9·9 g) was obtained and on analysis it was found to contain: Al, 7·92; OPr^i, 32·73%; $Al(OPr^i)_2(C_{11}H_{23}COO)$ requires: Al, 7·83; OPr^i, 34·3%.

The product reacted rapidly with atmospheric moisture, evolving isopropanol and forming a white brittle coating, but this hydrolysis did not go to completion due to the protective action of the coating.

Aluminium monoisopropoxy dilaurate

Benzene (80 c.c.) was distilled into a mixture of aluminium isopropoxide (2·7 g) and lauric acid (5·3 g) (molar ratio of isopropoxide to acid = 1 : 2). The isopropanol distilled out azeotropically in nearly one hour was estimated to be 1·5 g against the theoretical value 1·52 g. A highly viscous rubber-like mass was obtained which on analysis gave: Al, 5·7; OPr^i, 12·13%; Calc. for $Al(OPr^i)(C_{11}H_{23}COO)_2$: Al, 5·57; OPr^i, 12·18%.

[5] R. C. MEHROTRA *J. Ind. Chem. Soc.* **30**, 585 (1953).

The hydrolysis of this compound in moist air is much slower than that of $Al(OPr^i)_2(C_{11}H_{23}COO)$. When completely hydrolysed, it became a fine white powder.

Aluminium di-isopropoxy monostearate

Benzene (60 c.c.) was distilled into a mixture of aluminium isopropoxide (1·94 g) and stearic acid (2·2 g) in the molar ratio 1 : 1. The mixture was refluxed in a bath at 130° and the isopropanol-benzene azeotrope was fractionated and collected within one hour; it was found to contain 0·5 g of isopropanol, compared with the theoretical value of 0·57 g. A highly viscous or pasty mass was obtained which on analysis was found to contain: Al, 6·32; OPr^i, 26·7%; $Al(OPr^i)_2(C_{17}H_{35}COO)$ requires: Al, 6·29; OPr^i, 27·57%.

Aluminium monoisopropoxy distearate

Benzene (50 c.c) was distilled into the mixture of aluminium isopropoxide (1·6 g) and stearic acid (4·47 g); in the molar ratio of 1 : 2. It was refluxed in a bath temperature 140° and the benzene-isopropanol azeotrope was collected in nearly one hour; it was found to contain 0·9 g of isopropanol compared with the theoretical value of 0·94 g. A sticky and opaque mass was obtained which on analysis gave: Al, 4·19; OPr^i, 7·9%; $Al(OPr^i)(C_{17}H_{35}COO)_2$ requires: Al, 4·15; OPr^i, 8·78%.

Aluminium dichloride monolaurate

3 g of acetylchloride were distilled to a solution of aluminium di-isopropoxy monolaurate (8·0 g) in benzene (50 c.c.). This mixture was refluxed in a bath at 100° for nearly two hours. The volatile fractions were removed by distillation at ordinary pressure. The product was finally dried by heating in a bath at 50° under reduced pressure (4 mm). A pale yellow viscous liquid was obtained, which on analysis was found to contain: Al, 8·8; Cl, 21·8%; $AlCl_2(C_{11}H_{23}COO)$ requires: Al, 9·07; Cl, 23·5%.

This reacted rapidly with atmospheric moisture, evolving HCl and forming a white brittle coating. The hydrolysis, however, did not go to completion due to the protective action of the coating.

Aluminium monochloride dilaurate

Aluminium mono-isopropoxy dilaurate (4 g) was dissolved in benzene (40 c.c.) and acetyl chloride (nearly 3 g) was distilled into this solution. It was refluxed in a bath at 110° for nearly two hours and the volatile fractions were removed completely as before. A pale yellow extremely viscous liquid was obtained which on analysis was found to contain: Al, 6·02; Cl, 7·1%; Calc. for $AlCl(C_{11}H_{23}COO)_2$: Al, 5·85; Cl, 7·68%.

This product was susceptible to hydrolysis, as was the dichloro-soap.

Reaction between aluminium di-isopropoxy monostearate and acetic anhydride; an attempt to prepare aluminium diacetoxy monostearate

Aluminium di-isopropoxy mono-stearate (3·5 g) was dissolved in benzene (20 c.c.) and acetic anhydride (3·5 g) was distilled into the solution. At once the reaction mixture became very hot and viscous. A white gelatinous mass was formed at first. On keeping this mixture at room temperature for nearly two hours, this mass gradually dissolved and the reaction mixture became mobile. It was now refluxed in a bath at 120° for nearly two hours, when a white insoluble substance was formed which was left overnight. The filtration was difficult due to the gelatinous nature of the precipitate. Nearly 20 c.c. of fresh benzene were, therefore, added to it and the white mass was filtered. The residue was dried under reduced pressure, giving finally a white powder which on analysis was found to contain: Al, 9·86%; a mixture of $Al(OAc)_2(C_{17}H_{35}COO)$ and $Al(OAc)_3$ in the molar ratio of 1 : 2 requires: Al, 9·66%.

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LETTERS TO THE EDITORS

Controlling rare-earth separations by means of varying resin column operating temperatures*

(*Received* 3 *June* 1956)

UNDER constant operating conditions, the elution method of separating rare earths on a cation resin column gives rise to a characteristic pattern wherein each peak or band as it is eluted tends not only to be broader (lower in rare-earth concentration), but also relatively further away from its immediate predecessor than the latter was from the band ahead of it. As a result, when conditions are chosen such that satisfactory separation of the earlier bands is attained, the later ones are found to be inordinately slow in eluting, and are in unsatisfactorily low concentration when they are obtained. As a means of overcoming these difficulties, NERVIK[1] has described a "gradient elution" technique which employs special mixing equipment so that the pH of the eluting solution can be gradually raised during the progress of a separation run, thus causing a corresponding increase in the concentration of the complex-forming organic acid anion responsible for eluting the bands down the column. Increasing the amount of this anion causes the slower bands still on the bed to elute more rapidly than would otherwise be the case, the net effect being to shorten the overall time required to complete the separation, and to produce a series of peaks more uniform in spacing and in rare-earth concentration.

Literature data are limited relative to the effect of higher temperatures on the dissociation constants of the organic acids usually used as eluting agents in these rare-earth separations, but it is apparent that, in general, they are decreased. (For glycolic acid in the 0 to 50°C range, NIMS[2] has shown that the dissociation reaches a maximum value at 30·2°C, and then falls off steadily above this temperature.) Since this is so, it should be possible to obtain an effect similar to that described by NERVIK by starting the separations run at a high operating temperature and then allowing the column to cool slowly during the period of the experiment, thus again increasing the concentration of the complex-forming anion as the run progresses. Fig. 1 shows the results of three experiments which demonstrate that this technique does give rise to a type of gradient elution effect.

EXPERIMENTAL

A 5-cm × 2-mm jacketed column of −400 mesh NH_4^+ Dowex-50 cation exchange resin was used. The eluting solution for all runs was 0·1 M α hydroxy isobutyric acid[3] having a room-temperature pH of 4·77. The same pressure head was maintained on the eluting solution feed burette for each of the three runs, the resulting flow rates being about 0·25 ml/min/cm² for the 25°C run, 1·2 ml/min/cm² at 95°C, and, as the column cooled, at various rates between these two values for the variable temperature experiment. All other conditions were the same for the three runs. Temperatures were read from a thermometer having its bulb in the eluting solution immediately over the surface of the resin bed. Total operating times for the three runs to the points shown in the figure were 160 minutes, 820 minutes, and 360 minutes respectively.

As marked on the figure, curve 1*a* represents the experimental result for a separations run wherein the operating temperature was held at 25°C throughout, and curve 1*b* a run where the temperature was constant at 95°C. In the third experiment (curve 1*c*) the initial temperature of 93°C was held constant until the first band started to elute from the column, then the latter was allowed to cool,

*Based on work performed under the auspices of the U.S. Atomic Energy Commission.

[1] W. E. NERVIK *J. Phys. Chem.* **59**, 690 (1955).
[2] L. F. NIMS *J. Amer. Chem. Soc.* **58**, 987 (1936).
[3] G. R. CHOPPIN, B. G. HARVEY, and S. G. THOMPSON *J. Inorg. Nucl. Chem.* **2**, 66 (1956).

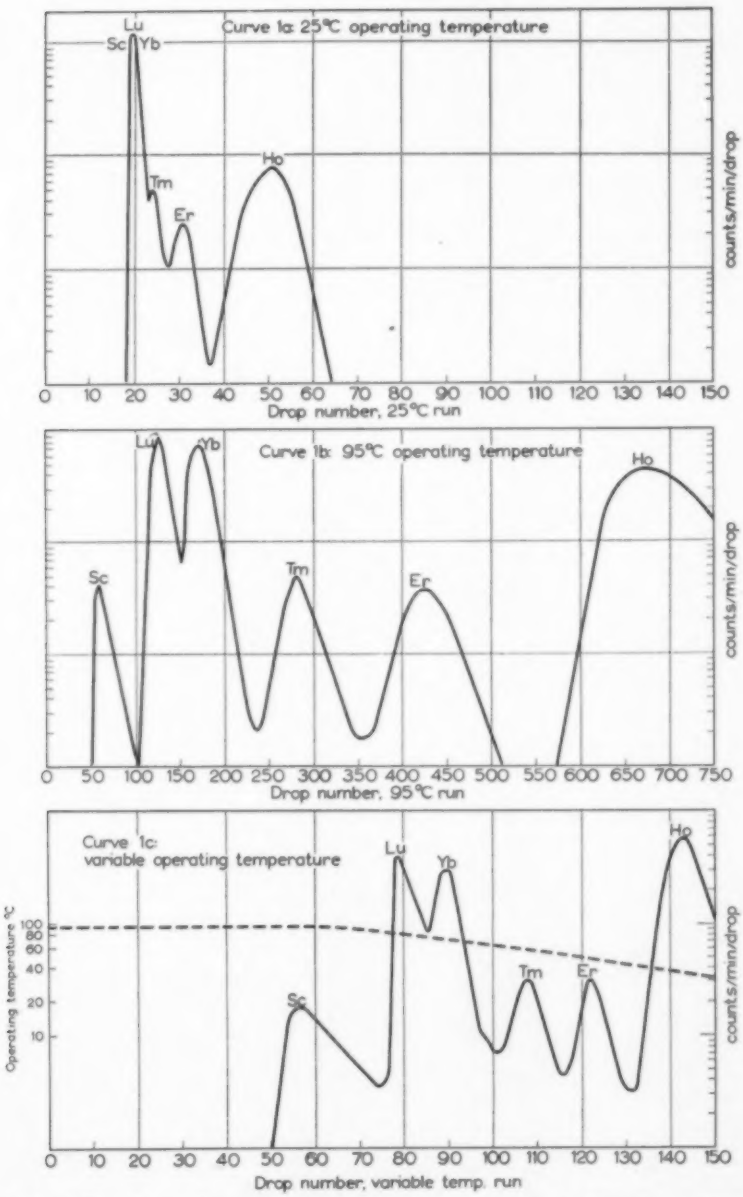

FIG. 1.—Effect of operating temperature on the elution of rare earths from Dowex-50 with ammonium α-hydroxy isobutyrate.

the actual temperature drop being shown by the dotted line over curve 1*c*. It will be seen that this latter run retains much of the separations efficiency of the 95°C experiment, while requiring markedly less total operating time. (The relatively dilute eluting solution concentration used was chosen so that some separation would be seen in the 25°C experiment, although, as a result, the operating times for the other two runs were longer than would be desirable in normal practice. Both of these runs, of course, could be shortened by using an eluant having a higher initial concentration of isobutyrate ion. Presumably the variable temperature results might also be improved by holding the initial temperature for a slightly longer period to increase the sharpness of separation of the initial bands, followed by a more rapid cooling of the column than is shown in Fig. 1*c* so as to cut down the total separation time.)

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The reaction of cerium(III) with 2-methyl-8-quinolinol

(*Received* 13 *August* 1956)

In the course of investigating the analytical properties of the rare earth metal chelates of 2-methyl-8-quinolinol (8-hydroxyquinaldine, methyl-oxine), it was found that cerium(III) reacted differently than the other trivalent rare earth metal ions.[1] 2-Methyl-8-quinolinol formed yellow coloured insoluble chelates with the trivalent rare-earth metal ions which corresponded to the general formula, $M(C_{10}H_8NO)_3$, where M is the rare-earth element. With cerium(III), however, a purple coloured chelate precipitated out of solution which corresponded to the formula, $Ce(C_{10}H_8NO)_4$.

The cerium chelate was formed under the following experimental conditions. To a solution containing 0·3 to 0·4 g of $CeCl_3 \cdot 6H_2O$ in 150 ml of water were added 10 ml of 2 N $HC_2H_3O_2$ and 10 ml of 2 M $NH_4C_2H_3O_2$ solution. A slight excess of 2-methyl-8-quinolinol solution (4% (W–V) in 2 N $HC_2H_3O_2$) was added and the pH of the solution adjusted to 7–8 with 2 N NH_4OH solution. On the introduction of the NH_4OH a yellow-brown coloured precipitate first formed which darkened in less than a minute to a purple colour. The solution was allowed to stand at room temperature for several hours, then filtered through a sintered porcelain crucible, washed twice with water and air-dried for 24 hours at room temperature. Samples of the air-dried chelate were ignited to CeO_2 in tared platinum crucibles at 650°C and gave the following results: for the chelate found, 22·36, 22·41% CeO_2; calculated for Ce $(C_{10}H_8NO)_3$, 22·27% CeO_2; calculated for $Ce(C_{10}H_8NO)_3$, 28·00% CeO_2. The thermal decomposition of the chelate on the thermobalance will be discussed elsewhere.[1]

Since this reaction appears to be specific for cerium(III), the absorption spectra of the chelate in various solvents was studied as a possible analytical method.

Fig. 1 shows the absorption curves, taken with a Beckman, Model DU, spectrophotometer, of the chelate in $CHCl_3$ and 2 N $HC_2H_3O_2$ solutions. All measurements were made in 1·00-cm silica cells. The $CHCl_3$ solutions gave a broad absorption peak at 485 mμ, a sharper peak at 305 mμ, and small partially obscured peak at 330 mμ. The 485-mμ peak can be attributed to the $Ce(C_{10}H_8NO)_4$ chelate. A quantitative analytical application does not seem feasible, because the 485-mμ peak gradually decreased on standing. Apparently, the chelate slowly decomposes in this solvent.

The $Ce(C_{10}H_8NO)_4$ chelate is completely dissociated in 2 N $HC_2H_3O_2$ as shown in the absorption curve. There are absorption maximas at 345 and 315 mμ, but the 485-mμ peak is absent. For comparison with the trivalent rare-earth chelates, the absorption spectra of $La(C_{10}H_8NO)_3$ in $CHCl_3$ is also given. Only one prominent absorption peak appears and that is at 305 mμ.

[1] W. W. Wendlandt, to be published.
[2] J. P. Phillips *Chem. Rev.* **56**, 276 (1956).

Cerium(III) also forms a tetravalent chelate with 8-quinolinol corresponding to the formula, $Ce(C_9H_6NO)_4 \cdot 2H_2O$.[3] The trivalent chelate, $Ce(C_9H_6NO)_3$, can also be prepared if precipitation is carried out from tartrate buffered solutions[4] or by homogeneous precipitation methods.[5]

The conversion of cerium(III) to cerium(IV) in this reaction has been attributed to the oxidizing action of the 8-quinolinol molecule.[2] Similar reactions have been observed in which iron(II) is oxidized to iron(III) ion and chromium(II) to chromium(III). It appears that this is a false interpretation because the oxidizing agent is atmospheric oxygen. This was shown in the case of the

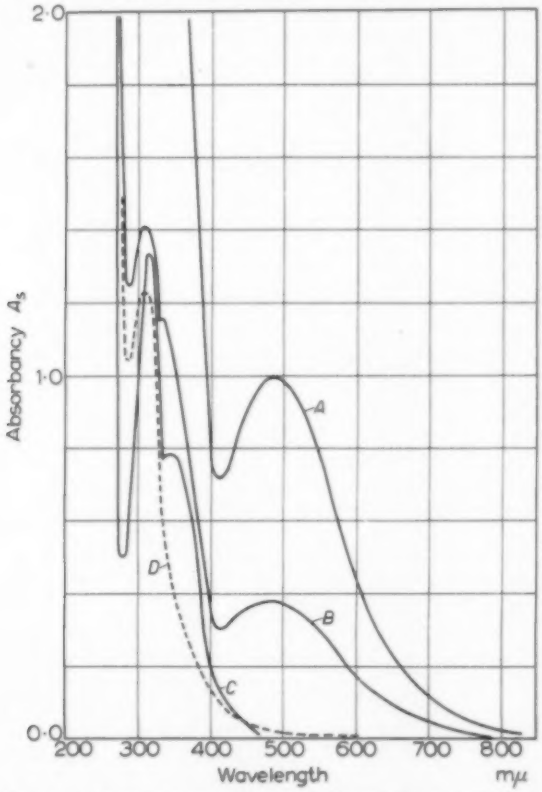

FIG. 1.—The absorption spectra of the 2-methyl-8-quinolinol chelates.
Curve A. $2{\cdot}97 \times 10^{-4}$ M $Ce(C_{10}H_8NO)_4$ in $CHCl_3$.
Curve B. $1{\cdot}24 \times 10^{-4}$ M $Ce(C_{10}H_8NO)_4$ in $CHCL_3$.
Curve C. $1{\cdot}19 \times 10^{-4}$ M $Ce(C_{10}H_8NO)_4$ 2 N $HC_2H_3O_2$.
Curve D. $1{\cdot}74 \times 10^{-4}$ M $La(C_{10}H_8NO)_3$ in $CHCl_3$.

cerium(III) 2-methyl-8-quinolinol reaction by conducting the precipitation in a closed system under nitrogen. The precipitated chelate was a yellow-brown colour, characteristic of the trivalent rare earth chelates, and did not revert to the purple coloured chelate even on standing for four hours. On exposing some of the moist yellow-brown chelate to air, the colour rapidly darkened to a deep purple, indicating oxidation to the tetravalent oxidation state by atmospheric oxygen.

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[3] T. I. PIRTEA *Bul. Chim. Soc. Române Chim.* **39**, 83 (1937–8).
[4] R. BERG and E. BECKER *Z. anal. Chem.* **119**, 1 (1940).
[5] W. W. WENDLANDT *Anal. Chim. Acta* **15**, 109 (1956).

Deposition of activities from thoria slurries

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In processes involving the agitation of stainless-steel, zirconium, and zircalloy discs in aqueous thoria slurries, it has been found that in general a preferential plating out of the radium daughters of natural thorium occurs.

Stainless-steel and zirconium discs were agitated in thoria slurry at 100°C for 1 hour. Stainless-steel and zircalloy discs were agitated in thoria slurry of concentration 1000 g of thoria per 1000 g

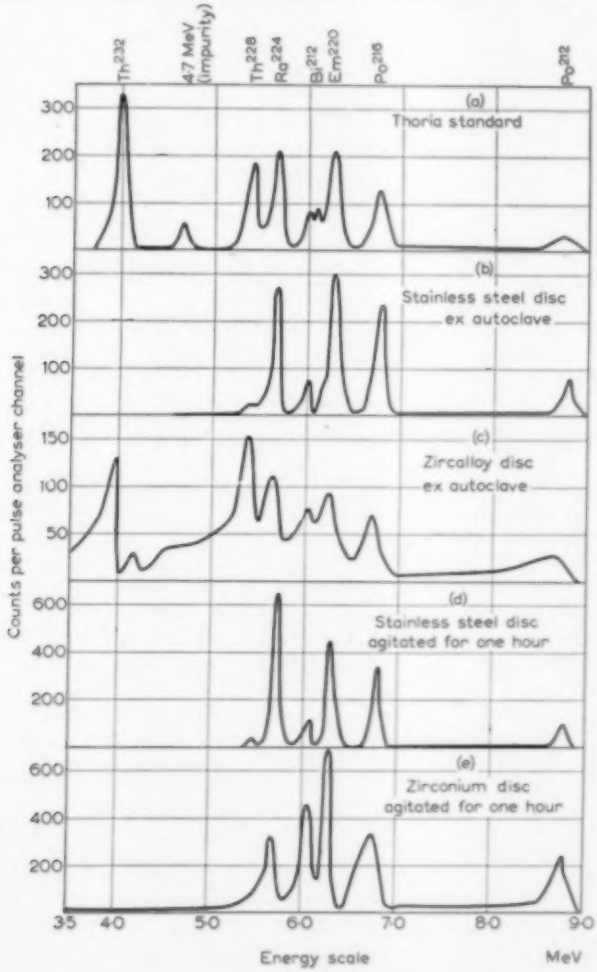

Fig. 1.—Alpha-pulse analyses of activities deposited from thoria slurries.

of water at 300°C for 1 week in an autoclave. All these discs were washed for 1 hour in a Soxhlet extractor, to ensure removal of thoria adsorbed on to the discs. As a standard for comparison, some thoria was deposited directly from thorium nitrate solution on to a stainless-steel disc and ignited to thoria. The deposition products were α-pulse analysed in a gridded ion chamber.[1] The poor resolution obtained with all the sources was due to source thickness. The results are shown in Fig. 1.

Confirmation of the preferential deposition of Ra^{224} and its daughters on to stainless-steel discs was obtained by α-counting three such discs over a period of time and observing the decay. This corresponded to the 3·64-day half-life of Ra^{224}. Ra^{228} would be plated out in equilibrium with Ra^{224}, but as it is a β-emitter, it would not be detected in the equipment used. However, it is to be expected that over a period of time the α-emitters from Th^{228} to Po^{212} would build up to equilibrium at a rate corresponding to the half-life of the β-emitter Ra^{228} (6·7 y). Additional confirmation was obtained by refluxing for 1 hour a stainless-steel disc in a radium chloride solution (primarily Ra^{226}). On analysis, this sample showed a characteristic radium decay scheme containing the α-emitting daughters of Ra^{226} and Ra^{224}.

Further, an attempt was made to hold back the radium isotopes present in thoria slurry. Stainless-steel and zirconium discs were refluxed for 16 hours in a thoria slurry of composition: 50 g ThO_2 + 50 g $BaCl_2$ + 100 ml H_2O, the barium chloride acting as a hold-back carrier for the radium present in the slurry. For both discs, the α-pulse analyses showed the presence of Th^{228} and all α-emitting daughters, but with a major contribution of Po^{212} and Bi^{212}, indicating that the radium isotopes were to some extent held back.

To date, the mechanism by which radium isotopes are preferentially deposited on metals from aqueous thoria slurries has not been elucidated. Radium metal, as such, is not deposited because of its very high electrode potential (−2·7 V). The activities deposited are not due to a physical adsorption of a water-soluble radium compound, since the discs were adequately washed in a Soxhlet extractor before α-pulse analysis. Even though conductivity water containing CO_3^{--}, HCO_3^-, and OH^- ions in equilibrium was used in all the systems studied, the observed activities cannot be due to the deposition of insoluble radium carbonate, since the effects have also been observed with thoria slurries made 1 N with respect to HCl and HNO_3. It is possible that exchange reactions via surface hydroxyl groups on the metal surface and recoil effects may contribute to the total deposition.

BATES and ROGERS[2] reported the deposition of minute traces of radium and of polonium present in RaD solution when a copper disc was rotated in a warm solution of RaD. This solution had been separated from a parent solution of radium chloride which had been freed from lead by precipitation.

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[1] K. M. GLOVER A.E.R.E. C/R 2091 (1956).
[2] L. F. BATES and J. S. ROGERS *Proc. Roy. Soc.* **A105**, 360 (1924).

* Australian Atomic Energy Commission.

ANNOUNCEMENT

In order to simplify the publishing mechanics and speed up the rate of publication of individual papers, the *Journal of Inorganic and Nuclear Chemistry* will, in future, be published in volumes containing four issues each, and issues will follow each other at approximately six-week intervals. The publishing date will not be rigidly fixed, since it is the policy of the publishers to publish an issue as soon as it is ready so that the publishing delay may be cut down to a minimum, in the interests of contributors. Each volume, of course, will continue to contain approximately 400 pages, but will now be contained in four issues instead of six.

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THE ALPHA HALF-LIFE OF AMERICIUM-241

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Abstract—The preparation of three compounds of americium—AmO_2, $Am_2(SO_4)_3$, and anhydrous $AmCl_3$—is described. These compounds have been used in the determination of the alpha half-life of Am^{241}. A value of $7{\cdot}187 \pm 0{\cdot}007 \times 10^6$ α/min/μg was obtained for the specific activity, from which the half-life is calculated to be $458{\cdot}1 \pm 0{\cdot}5$ years.

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THE first determination of the alpha half-life of Am^{241} was carried out by B. B. CUNNINGHAM,[1] using a few micrograms of this isotope. Americium trifluoride was ignited in air to the oxide of americium, AmO_2, and weighed on a quartz fibre microbalance. A value of 498 years was obtained and a probable error of $\pm 5\%$ assigned to this value because of impurities and uncertain stoichiometry. Two subsequent determinations yielded figures that gave 510 ± 22 years as the best value from all the determinations. Later unpublished work by the same author gave a value of 490 ± 14 years.[2] The specific activity of 5-μg samples of AmO_2 was measured by B. G. HARVEY[3] and the half-life reported as 470^{+5}_{-10} years. Spectrographic analysis of the americium showed the presence of up to 1% by weight of impurities.

EXPERIMENTAL

Because of the large quantities of fission products and the high proportion of rare earths in the fission products, the separation of americium from irradiated uranium would be extremely difficult. The starting product was therefore plutonium which had been separated from fission products. Pu^{241} (half-life 13 years) was allowed to decay and the Am^{241} extracted as follows, using glove-box handling techniques: a considerable amount of plutonium in dilute nitric acid, which contained Pu^{241} and hence its β-decay product Am^{241}, was treated with the solvent tributyl phosphate. This extracted most of the plutonium, some of the uranium, but not the americium. After a series of such extractions, the aqueous phases were combined and used as the starting material.

Final separation of americium from plutonium was carried out using an anion-exchange method. Americium, together with the plutonium impurity, was placed on to a column of DeAcidite-FF in 80% nitric acid, and americium, which is not adsorbed, was washed from the column with a similar nitric acid solution. Alpha-particle pulse analysis on an americium source indicated that no plutonium remained as impurity. Other impurities such as iron, calcium, magnesium, aluminium, boron, and lead were separated on a cation-exchange column. Final traces of aluminium were removed by the precipitation of pink americium trihydroxide with a few drops of a strong solution of sodium hydroxide, aluminium remaining in solution as the aluminate. Silica was removed by fuming the americium in sulphuric acid with hydrofluoric acid in a platinum basin. Analysis for uranium by fluorimetric assay showed that the americium contained less than 0·02% of uranium. The americium was stored in a closed platinum tube.

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[1] B. B. CUNNINGHAM *N.N.E.S.* Vol. 14B. Paper 19.2.
[2] B. B. CUNNINGHAM and S. G. THOMPSON (unpublished) quoted by G. T. SEABORG and I. PERLMAN *Rev. Mod. Phys.* **20**, 585 (1948).
[3] B. G. HARVEY *Phys. Rev.* **85**, 482 (1952).

DETERMINATION OF THE HALF-LIFE

Americium oxide (AmO_2)[4]

Black americium oxide was prepared by heating the nitrate in air to 890°C. A thermogravimetric study of AmO_2 showed that no loss in weight occurred on heating the oxide from 800 to 900°C and that there was no uptake of moisture by the oxide on cooling to room temperature. X-ray analysis of the oxide prepared at 890°C showed that only a single phase was present, cubic in structure and isomorphous with ThO_2, UO_2, and PuO_2. The edge of the cubic cell was 5·373 ± 0·005 kX units.

From a stock solution of americium in nitric acid, a weighed sample was transferred to a platinum crucible, converted to the oxide at 890°C, and weighed as AmO_2. A second weighed sample from the stock solution was diluted to 25 ml in a standard flask, and from this, aliquots of 10 μl were pipetted with an Agla microburette on to clean platinum counting trays. To obtain a uniform film for counting, a drop of a spreading agent was added to each sample before evaporation. The aliquot was evaporated to dryness and heated to 600°C to remove organic matter. Three sources were prepared and counted in a low-geometry proportional counter[5] (geometry factor 721·2 ± 0·8). The counts for replicate sources agreed to within the statistics of counting (±0·1%).

Three separate determinations of the specific activity were made by this method, three sources being prepared in each case. The results are given in Table 1.

TABLE 1

Experiment	Specific activity	Half-life
1	$7·146 \times 10^6$ α/min/μg*	460·6 ± 0·9 years
2	$7·129 \times 10^6$ α/min/μg	461·7 ± 0·9 years
3	$7·132 \times 10^6$ α/min/μg	461·5 ± 1·2 years

Mean value 461·2 ± 0·6 years

* This is the weight of Am^{241} assuming the compound to be stoichiometric AmO_2 and of purity 99·85 ± 0·04%.

Spectrographic analysis of the americium gave a purity of 99·85 ± 0·04%. The only impurity detected was magnesium (0·15 ± 0·04%). The geometry of the counter was measured to within 0·15 %. Counter 18 was identical with those (counters 12 and 13) used in the comparison and counting experiment at Berkeley Laboratory.[6] A standard source was counted in counter 18 and counter 12. The agreement was to within the statistics of counting (±0·1%). Errors in duplicate weighings were ±0·1%. The errors given for the three separate experiments (Table 1) are computed from all the known sources of error. The error given for the final result was obtained from the individual errors. A weighted mean value was used for the half-life because the error in experiment 3 was greater than the errors in experiments 1 and 2. Two other possible sources of error are that (1) undetected impurities are present (2) the AmO_2 may not be stoichiometric.

[4] G. R. HALL and T. L. MARKIN *J. Inorg. Nucl. Chem.* **2**, 202 (1956).
[5] R. HURST and G. R. HALL *Analyst* **77**, 790 (1952).
[6] K. M. GLOVER and G. R. HALL *Nature* **173**, 991 (1954).

Americium sulphate ($Am_2(SO_4)_3$)

White americium sulphate was prepared by heating americium in sulphuric acid solution to a temperature of 550–650°C in air. A thermogravimetric study of $Am_2(SO_4)_3$ showed that no loss in weight occurred between 550–650°C. Further heating of the sulphate to 800°C caused a slow decrease in weight due to formation of AmO_2 (Fig. 1). X-ray analysis showed that the final product was identical with the AmO_2 prepared by

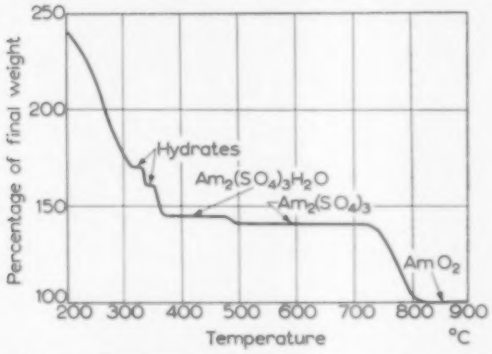

FIG. 1.—Thermogravimetric curve for americium sulphate.

heating the nitrate to 800°C. The equivalent weight of 384 for the compound prepared by heating americium in sulphuric acid to 550–650°C was calculated by comparing the weight of this compound with the weight of the final product (AmO_2).

The theoretical equivalent weight for $Am_2(SO_4)_3$ is 385. No uptake of moisture occurred on allowing the sulphate to cool to room temperature. The thermogravimetry of $Am_2(SO_4)_3$ was compared with that of gadolinium sulphate, prepared by

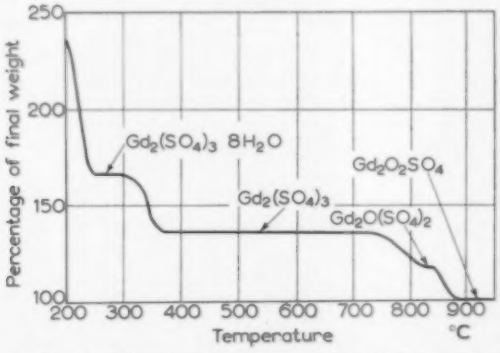

FIG. 2.—Thermogravimetric curve for gadolinium sulphate.

heating gadolinium oxide in sulphuric acid to 360–740°C. Further heating caused the formation of $Gd_2O(SO_4)_2$ at 830°C and $Gd_2O_2SO_4$ at 880°C (Fig. 2). On cooling to room temperature, $Gd_2O_2SO_4$ took up moisture and the final weight corresponded to the formula $Gd_2O_2SO_4 \cdot \frac{1}{2}H_2O$.

A method due to FRITZ and YAMAMURA[7] was used to analyse $Am_2(SO_4)_3$ for sulphate. The compound was dissolved in approximately 10 ml of water, and the

[7] J. S. FRITZ and S. S. YAMAMURA ISC-540 (1954).

americium removed by passing through a fine-grain Zeocarb-225 column. The sulphate was titrated with barium perchlorate in the presence of 80% alcohol, using thorin (1-(*o*-arsenophenylazo)3,6-disulphonic acid) as indicator. Analysis of $Am_2(SO_4)_3$ showed that the sulphate content was 99·7 ± 0·4% of the theoretical value.

For the specific activity determination, 7 mg of americium in 0·5 ml of concentrated sulphuric acid was transferred to a weighed platinum crucible, evaporated to dryness, and heated to 600°C. The final product was weighed as $Am_2(SO_4)_3$, dissolved in 0·001 M nitric acid, and diluted to 250 ml in a standard flask. Counting sources were prepared from 10-μl aliquots of this solution as before and counted in the low-geometry proportional counter.

Three separate determinations of the specific activity were made by this method, and the results are shown in Table 2.

TABLE 2

Experiment	Specific activity	Half-life
4	7·183 × 10^8 α/min/μg*	458·2 ± 1·3 years
5	7·193 × 10^8 α/min/μg	457·6 ± 1·3 years
6	7·204 × 10^8 α/min/μg	456·9 ± 1·3 years

Mean value 457·6 ± 0·8 years

*This is the weight of Am^{241}, assuming the compound to be stoichiometric $Am_2(SO_4)_3$ and of purity 99·29 ± 0·05%.

Spectrographic analysis of the americium indicated a purity of 99·29 ± 0·05%. The only impurities detected were magnesium (0·55 ± 0·05%) and silicon (0·16%). Counts for replicate sources agreed to within the statistics of counting (±0·15%). Errors in duplicate weighings were ±0·1%.

Americium trichloride ($AmCl_3$)

S. FRIED[8] prepared a few micrograms of $AmCl_3$ for X-ray analysis, by the action of carbon tetrachloride on AmO_2 at 850–900°C.

$$AmO_2 + 2CCl_4 \rightarrow AmCl_3 + 2COCl_2 + \tfrac{1}{2}Cl_2.$$

This method was used to prepare milligram quantities of $AmCl_3$ for the specific activity determination after testing the apparatus (Fig. 3) by the preparation of UCl_4.

$$UO_2 + 2CCl_4 \xrightarrow{450\text{-}600^\circ C} UCl_4 + 2COCl_2$$

As UCl_4 and $AmCl_3$ are hygroscopic materials, an airtight dry-box was constructed. Air in the box was circulated through a cold trap in which water vapour condensed.

Approximately 100 mg of UO_2 were placed in the silica tube inside the reaction vessel and the apparatus was evacuated. Redistilled carbon tetrachloride (b.p. 76–77°C) was allowed to stand over $CaCl_2$ in tube *Q* (Fig. 3) for 24 hours and then distilled into tube *P*, thus ensuring that the CCl_4 was free from moisture. The reaction vessel was heated to 450°C, and with tap *A* closed, sufficient CCl_4 vapour was admitted to the

[8] S. FRIED *J. Amer. Chem. Soc.* **13**, 416 (1951).

reaction vessel to give a pressure of 4–5 cm of mercury. After several minutes, tap *A* was opened. A brown sublimate slowly appeared on the walls of the silica tube beyond the mouth of the furnace. This procedure was repeated until approximately 100 mg of UCl_4 had collected on the walls of the tube. The UCl_4 became green on cooling; taps *D* and *E* were then closed and the greased joint between *D* and *E* was opened. The reaction vessel was transferred to the dry-box. The sublimate of UCl_4 was scraped from the walls of the silica tube into a weighing bottle having a greased ground-glass joint. The bottle was taken from the dry-box and weighed. Many samples of UCl_4 were analysed for uranium and chlorine thus: the uranium content

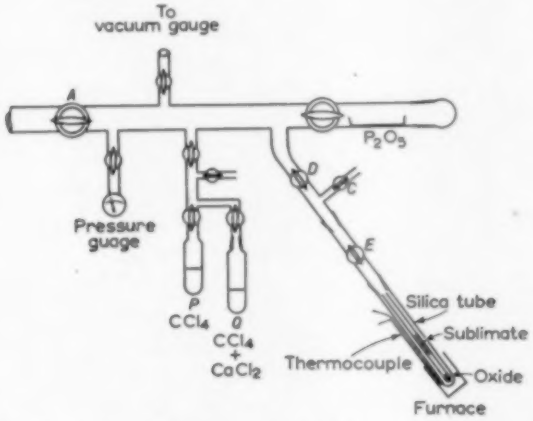

FIG. 3.—Apparatus for the preparation of americium trichloride.

was determined by dissolution in an excess of ferric alum solution, the ferrous ion produced being titrated potentiometrically with potassium dichromate. Chloride was titrated potentiometrically with silver-nitrate solution. The results showed that the UCl_4 contained 99·9 ± 0·2% of the theoretical weight of uranium and 99·8 ± 0·2% of the theoretical weight of chlorine.

Americium trichloride was prepared in a similar manner. A pale pink sublimate of $AmCl_3$ appeared beyond the mouth of the furnace. As only a few milligrams of $AmCl_3$ were prepared, the section of the silica tube containing the sublimate was cut from the remainder of the tube in the dry-box and weighed in a sealed bottle. The pink sublimate of $AmCl_3$ was dissolved in nitric acid, the tube washed, dried, heated to 600°C, and weighed. Americium trichloride, unlike plutonium trichloride, was found to be insoluble in water but dissolved readily in nitric acid. The solution of $AmCl_3$ was diluted to 25 ml in a standard flask and 10-μl aliquots were transferred to platinum trays for counting. Three separate determinations of the specific activity were made by this method. 20 ml of the solution was removed from the standard flask and titrated potentiometrically for chloride with 0·01 M silver-nitrate solution. The results of these determinations are shown in Table 3.

Spectrographic analysis showed the presence of 0·2% magnesium and 0·2% aluminium in the original americium solution. Counts for replicate sources agreed to within the statistics of counting (±0·1%). Errors in weighings were ±0·1%.

TABLE 3

Experiment	Specific activity	Half-life	Chloride ion concentration as a percentage of theoretical conc.
7	$7{\cdot}174 \times 10^6$ α/min/μg*	458·8 ± 1 year	99·7 ± 0·4
8	$7{\cdot}191 \times 10^6$ α/min/μg	457·7 ± 1 year	100·1 ± 0·4
9	$7{\cdot}176 \times 10^6$ α/min/μg	458·6 ± 1 year	100·1 ± 0·4

Mean value 458·4 ± 0·6 years

* This is the weight of Am^{241}, assuming the compound to be stoichiometric $AmCl_3$.

DISCUSSION

The values calculated for the alpha half-life of americium-241, using the compounds $Am_2(SO_4)_3$ and $AmCl_3$, are in good agreement, but the value obtained using the compound AmO_2 is outside the experimental error. In order to obtain a value for the half-life from the results of the experiment involving americium oxide, comparable with the value for the half-life obtained from the americium sulphate and americium trichloride experiments, it would be necessary for the oxide, prepared at 890°C, to have the formula $AmO_{2\cdot1}$. WELCH[9] has shown that plutonium oxide has an oxygen excess at 900°C, but is stoichiometric PuO_2 at 1200°C. The weighted mean values of $7{\cdot}187 \pm 0{\cdot}007 \times 10^6$ α/min/μg for the specific activity and 458·1 ± 0·5 years for the alpha half-life of americium-241 are the results obtained from the experiments using the compounds $Am_2(SO_4)_3$ and $AmCl_3$.

The values for the half-life of plutonium-241, recorded by MACKENZIE, LOUNSBURY, and BOYD[10] (13·06 ± 0·2 years) and ROSE and MILSTED[11] (12·77 ± 0·28 years), which depend upon the half-life of americium-241, are increased to 13·32 ± 0·12 years and 13·04 ± 0·28 years respectively.

Acknowledgements—The authors wish to thank Dr. J. MILSTED for carrying out the main separation of americium from plutonium, Mr. F. T. BIRKS for many spectrographic analyses, and Dr. E. WAIT, who examined the X-ray diffraction photographs.

[9] G. A. WELCH Private communication.
[10] D. R. MACKENZIE, M. LOUNSBURY, and A. W. BOYD *Phys. Rev.* **90**, 327 (1953).
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J. Inorg. Nucl. Chem., 1957, Vol. 4, pp. 143 to 145. Pergamon Press Ltd., London

HALF-LIFE OF Pu^{236}*

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(*Received* 12 *December* 1956)

Abstract—The half-life of the alpha emitter, Pu^{236}, was measured by a direct decay method. Corrections were applied for the alpha-emitting daughters of Pu^{236}. The results of three sets of data were: 2·855 yr, $s = 0{\cdot}009$ yr; 2·817 yr, $s = 0{\cdot}04$ yr; 2·836 yr, $s = 0{\cdot}021$ yr. The weighted average is 2·851 yr with $s = 0{\cdot}008$ yr.

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THE half-life of Pu^{236} has been reported by JAMES *et al.* to be $2{\cdot}7 \pm 0{\cdot}3$ yr.[1] They measured the half-life by directly following the alpha decay of plutonium separated from U^{235} which had been bombarded with helium ions, and of plutonium which had grown from the neptunium fraction from these bombardments. The measurements were complicated by the presence of other plutonium alpha emitters, particularly Pu^{238}, ($T_{1/2} = 86{\cdot}62$ yr[2]), and the accuracy of the half-life depended on the accuracy with which corrections for these could be made.

In the following experiments, very high-purity U^{235} was bombarded with deuterons in order to produce Pu^{236} as free of other plutonium alpha emitters as possible. The decay of several plutonium samples was then followed on a 2π methane flow proportional counter. Corrections were applied to the data for the contribution from the alpha-emitting daughters of Pu^{236}.

EXPERIMENTAL PROCEDURE

A sample of U^{235} (99·78% U^{235}) was bombarded with $<11{\cdot}5$ MeV deuterons in the Los Alamos Scientific Laboratory cyclotron to produce Pu^{236} by beta decay of 22-hr Np^{236} formed by the (d, n) reaction on U^{235}. The first chemical separation of the plutonium from neptunium was made within 6 hours after the end of bombardment in order to minimize the amount of Pu^{238} which would grow in from 2·1-day Np^{238} formed by the $(d, 2n)$ reaction on any U^{238} in the U^{235}.

Purification of the plutonium was accomplished by a series of reduced and oxidized LaF_3 precipitations, and by HI-HCl elutions from anion exchange resin columns.† In order to prepare a very clean sample, an aliquot of the purified plutonium fraction was evaporated on a tungsten strip and the plutonium was then vaporized *in vacuo* onto a 1-in.-diameter platinum disc. Alpha pulse analysis showed only the 5·75 MeV alpha group of Pu^{236} (Fig. 1). The sample, Pu^{236}-I, was then alpha-counted every two weeks in a 2π methane flow proportional counter over a period of nearly three years. Duplicate counts totalling 25,000–40,000 counts each were taken unless the spread was greater than 1%, in which case a third count was taken. Pu^{239} standards were counted on the same counter to check its performance.

* This work was done under the auspices of the U.S. Atomic Energy Commission.

† J-11 Collected Radiochemical Procedures (Radiochemistry Group J-11), LA-1721.

[1] R. A. JAMES, A. E. FLORIN, H. H. HOPKINS JR., and A. GHIORSO *The Transuranium Elements* (Ed. G. T. SEABORG, J. J. KATZ, and W. M. MANNING) McGraw-Hill, New York (1951), Paper No. 22.8, National Nuclear Energy Series, Plutonium Project Record, Div. IV, Vol. 14B Part II, p. 1604.

[2] D. C. HOFFMAN, G. P. FORD, and F. O. LAWRENCE *J. Inorg. Nucl. Chem.* (to be published).

Another sample of U^{235} (99·78%) was bombarded with ~21 MeV deuterons in the Argonne National Laboratory 60-in. cyclotron. The plutonium was separated from neptunium about 16 hours after the end of bombardment and was purified as in the first experiment. An aliquot was evaporated on a $1\frac{1}{8}$-in. platinum disc. Alpha pulse analysis of the sample showed only the alpha group of Pu^{236}. The decay of this sample, Pu^{236}-II, had been followed for about a year when an alteration was made in the counter which changed the counting rate of Pu^{236}-II by several per cent. Its decay was then followed for about another year. The data obtained before and after this change were analysed separately.

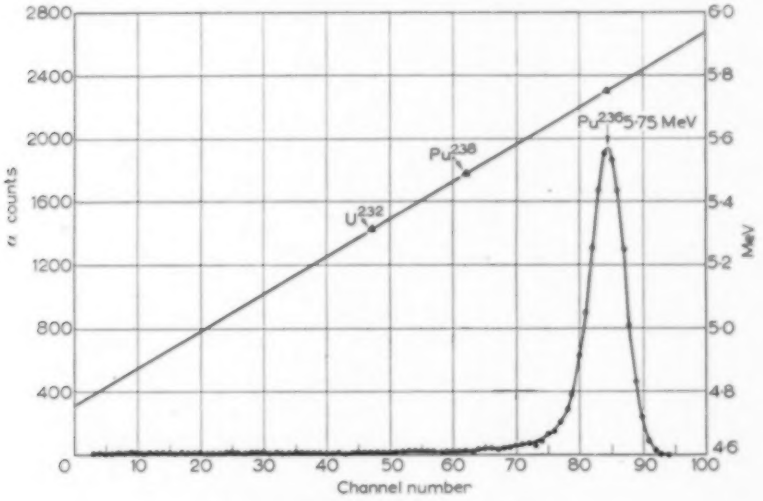

FIG. 1.—Alpha pulse analysis of Pu^{236}-I.

CALCULATION OF RESULTS

The observed counting rates were corrected for the contribution of the alpha-emitting daughters of Pu^{236} according to the Bateman[3] solution for the following decay series.

$$Pu^{236} \xrightarrow{\alpha} U^{232} \xrightarrow[73\cdot6\ yr^{[4]}]{\alpha} Th^{228} \xrightarrow[1\cdot90\ yr^{[3]}]{\alpha} Ra^{224} \xrightarrow[3\cdot64\ day^{[3]}]{\alpha} Em^{220}$$

$$\xrightarrow[54\cdot5\ sec]{\alpha} Po^{216} \xrightarrow[0\cdot158\ sec]{\alpha} Pb^{212} \xrightarrow[10\cdot64\ hr]{\beta^-} Bi^{212} \xrightarrow[60\cdot5\ min]{\alpha\,(33\cdot7\%)} Tl^{208}$$

$$Bi^{212} \xrightarrow[60\cdot5\ min\ (66\cdot3\%)]{\beta^-} Po^{212} \xrightarrow[3\cdot04\times10^{-7}\ sec]{\alpha} Pb^{208}\ \text{stable}$$

$$Tl^{208} \xrightarrow[3\cdot1\ min]{\beta^-}$$

It was assumed that all of the alpha emitters after Ra^{224} were in equilibrium with it and, therefore, contributed three times the alpha activity of the Ra^{224}. Fig. 2 shows the observed and the corrected counting rates for Pu^{236}-I.

After the corrections to the counting data had been made, the data were submitted to a least-squares analysis. The decay equation is nonlinear in the decay constant, making it desirable to iterate the calculation by using the result of one least-squares calculation as the initial approximation for the next. This was done until there was no

change in the eighth decimal place. The iteration was feasible because an electronic data processing machine was used.

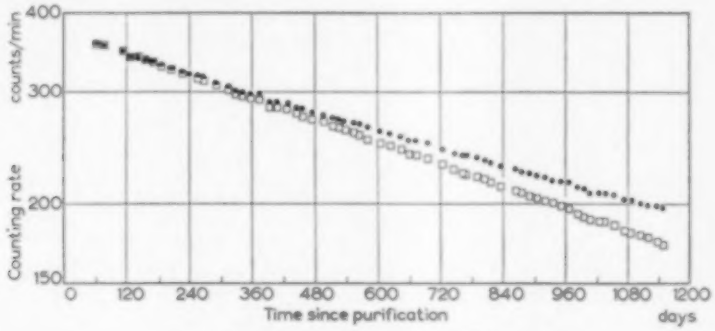

FIG. 2.—Decay curve for Pu^{236}-I.
● Observed counting rate.
□ Corrected for Pu^{236} daughters.

RESULTS

Sample I gave a half-life of 2·855 yr with standard deviation, s, of 0·009 yr. Sample II gave 2·817 yr, $s = 0{\cdot}04$ yr for the first set of counting data, and 2·836 yr, $s = 0{\cdot}021$ yr for the second set of counting data. All of the estimates of standard deviations were by external consistency.[6] The weighted average is 2·851 yr, $s = 0{\cdot}008$ yr.

Acknowledgements—It is a pleasure to acknowledge the assistance of Dr. JOHN NORTHRUP of the LASL cyclotron group in the preparation of a cyclotron target, the co-operation of other members of the LASL cyclotron group, and the members of the Argonne National Laboratory cyclotron group in providing the bombardments.

The authors are indebted to Dr. R. K. ZEIGLER and Dr. R. H. MOORE for the least-squares solution of the problem on IBM Electronic Data Processing Machines, Types 701 and 704.

We also wish to thank Mrs. LILLIAN JONES for alpha-counting the samples.

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DIE DARSTELLUNG VON STRONTIUM-90-FREIEM YTTRIUM-90 DURCH ELEKTROLYSE

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(*Received* 11 *December* 1956)

Abstract—The electrolytic deposition of ^{90}Y from weak aqueous nitric acid for the separation of carrier-free ^{90}Y from ^{90}Sr has been investigated. The ^{90}Y is deposited on the cathode with a yield of 90–98%. Through repetition of the electrolysis, ^{90}Y can be prepared with less than 10^{-4}% ^{90}Sr.

1. EINLEITUNG

Es besteht ein gewisses Interesse an der Verwendung von ^{90}Y in diesem oder jenem Arbeitsgebiet der angewandten Radioaktivität. Seine Eigenschaften—kurze Halbwertszeit (64 h), energiereiche β—Strahlung (2,2 MeV), keine γ Strahlung—sind z.B. für die Strahlentherapie recht günstig.[1] ^{90}Y ist auf zwei Wegen einfach zu gewinnen: (1) durch die Kernreaktion ^{89}Y (n, γ) und (2) als Tochtersubstanz des Spaltproduktes 28 a ^{90}Sr. Der erste Weg ist bei einer Anwendung in grossem Umfang ziemlich kostspielig und ergibt ausserdem keine trägerfreien ^{90}Y-Präparate. Der zweite Weg ist von diesen Nachteilen frei. Dafür gehört das ^{90}Sr zu den schädlichsten Radioisotopen; die für den menschlichen Körper insgesamt erlaubte Menge beträgt nur 1μ Curie.[2] Für die Abtrennung von ^{90}Y aus ^{90}Sr muss deshalb ein Verfahren verwendet werden, dass eine weitgehende Reinigung des ^{90}Y vom ^{90}Sr ermöglicht.

Die bekannten Verfahren zur ^{90}Y-Gewinnung benutzen die Fällung von $Sr(NO_3)_2$ durch konzentrierte Salpetersäure,[3] die Filtration des bei pH-Werten von 7–9 gebildeten ^{90}Y-Radiokolloids[4] oder die Extraktion des ^{90}Y mit Thenoyl-trifluoraceton in Benzol.[5] Weitere Möglichkeiten sind die Abtrennung an Kationenaustauschern,[6] Trennungen an Papierstreifen oder Cellulosesäulen[7] und die Elektrochromatographie.[8] Der Gehalt des ^{90}Y an ^{90}Sr wird bei der Nitratfällung durch konzentrierte HNO_3 mit 0,007% angegeben,[3] bei den übrigen Verfahren fehlt eine genauere Angabe des ^{90}Sr-Gehaltes. Diese Verfahren erschienen uns aus verschiedenen Gründen ungeeignet.

Eine grundsätzlich einfache Trennung zweier Substanzen ist die durch Elektrolyse, wenn es möglich ist, die erwünschte Substanz selektiv abzuscheiden. Die elektrolytische Abscheidung der unedlen Seltenen Erden als Metall gelingt nur aus wasserfreien basischen organischen Lösungsmitteln wie Äthylendiamin.[9] Bei Anwesenheit

* Diplomarbeit Mainz 1956.

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J. EINHORN, L. G. LARSSON, und I. RAGNHULT *Acta Radiologica* **43**, 298 (1955).

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selbst geringer Mengen Wasser tritt Hydrolyse ein und die Hydroxyde scheiden sich an Stelle der Metalle an der Kathode ab. Ebenso erhält man bei der Elektrolyse schwach saurer wässriger Lösungen kathodische Abscheidungen von Hydroxyden neben Hydroxydfällungen in der Lösung.[10,11] Dass die elektrolytische Abscheidung der Seltenen Erden auch in unwägbaren Mengen möglich sein muss, zeigen Arbeiten über das Verhalten von den Seltenen Erden sehr ähnlichen Elementen. So wurde Actinium aus schwach sauren wässrigen[12,13] wie alkoholischen Lösungen[14] kathodisch abgeschieden. Näher untersucht wurden die Bedingungen für die Abscheidung von Americium und Curium aus schwach salpetersaurer Lösung.[11] Nach diesen Untersuchungen schien es uns aussichtsreich, die Elektrolyse zur Abtrennung von ^{90}Y aus ^{90}Sr zu verwenden.

2. APPARATUR, METHODIK

Für die Elektrolyse wurde ein Rührstativ mit Heizplatte benutzt; mit der Kathode wurde gerührt. Bei festen Elektroden ist ein Magnetrührer verwendbar. Die Rührgeschwindigkeit betrug ungefähr 300 Umdrehungen pro Minute. Als Elektroden dienten ein Platinnetz als Anode und eine Platinspirale als Kathode oder zwei Platinspiralen, die Ergebnisse sind in beiden Fällen die gleichen. Die Verwendung von Kupfer und V2A-Stahl als Kathode wurde geprüft. Die Platinspiralen bestanden aus blankem Draht von 1,2 mm Durchmesser, der Durchmesser der Windungen betrug 5 bis 6 mm. Die Elektrolysezelle bestand aus einem 100 ml Becherglas, gewöhnlich wurden 30 ml Elektrolytlösung eingefüllt, für einige Versuche wurden grössere Gefässe und Volumina genommen. Als Spannungsquelle wurden zwei Akkumulatoren mit insgesamt 12 Volt verwendet.

Das $^{90}Y/^{90}Sr$ wurde aus Harwell bezogen. Es lag als Chlorid vor und wurde, um Chlorentwicklung während der Elektrolyse zu vermeiden, in das Nitrat überführt. Absolutbestimmungen des ^{90}Y-Gehaltes der angesetzten Stammlösung waren unnötig, es kam lediglich darauf an, das ^{90}Y immer unter den gleichen Bedingungen aufzuarbeiten und zu messen. Hierzu wurde ein Teil der ^{90}Sr-Lösung abpipettiert, auf 20 ml verdünnt und das ^{90}Y nach Zusatz von 5 mg Fe^{3+} und 10 mg Sr^{2+} mit karbonatfreiem Ammoniak an $Fe(OH)_3$ gefällt. Der $Fe(OH)_3$-Niederschlag wurde über ein Membranfilter abgesaugt, mit 2*n* heisser HCl gelöst und unter erneutem Zusatz von 10 mg Sr^{2+} wiederum gefällt. Im Filtrat der ^{90}Y-Fällung befand sich das ^{90}Sr mit 20 mg inaktivem Sr^{2+}. Dieses wurde mit Soda gefällt und auf einer Fritte gleicher Grösse wie beim ^{90}Y abgesaugt.

Für die Versuche zur elektrolytischen Abscheidung des ^{90}Y wurde ein abgemessener Teil der Stammlösung eingefüllt, vorsichtig zur Trockene gedampft und mit der Lösung aufgenommen, aus der elektrolysiert werden sollte. Um fest haftende Anteile wieder in Lösung zu bringen, wurde bis zum Sieden erhitzt und dann die erwünschte Temperatur eingestellt. Bei allen Versuchen lag das ^{90}Y bei der Abscheidung trägerfrei vor. Nach der Elektrolyse wurden die Elektroden unter Strom aus dem Elektrolyten herausgezogen, mit Alkohol oder Aceton gespült und die Aktivität mit 2 N HCl oder HNO_3 von den Elektroden abgelöst. Die Trennung der Aktivität erfolgte wie bereits beschrieben durch $Fe(OH)_3$- und $SrCO_3$-Fällung. Die vom $Fe(OH)_3$ mitgerissene ^{90}Sr-Menge lag innerhalb des Messfehlers der ^{90}Y-Messung, der dadurch der ^{90}Sr-Messung entzogene Anteil war vernachlässigbar klein. Die $^{90}SrCO_3$-Präparate enthielten unmittelbar nach der Trennung meist noch Reste an ^{90}Y, zur Ermittlung des ^{90}Sr-Anteils wurde bis zur Einstellung des Gleichgewichtes gewartet oder die Aktivität im Niederschlag durch Absorptionsmessungen mit Aluminiumabsorbern nach HARLEY-HALLDEN analysiert.[15] Zum Nachweis geringer ^{90}Sr-Mengen in starken ^{90}Y-Präparaten wurde die Hauptmenge des ^{90}Y durch eine weitere Elektrolyse abgetrennt. Der Elektrolyt enthielt nach der Elektrolyse noch etwa 5 bis 10% der vorliegenden Menge ^{90}Y mit 98 bis 99% des ^{90}Sr. Anschliessend erfolgte eine Y- Sr-Trennung durch $Fe(OH)_3$- und $SrCO_3$-Fällung. Die Aktivität des Niederschlags

[9] TH. MOELLER und P. A. ZIMMERMAN *Science* **120**, 539 (1954).
[10] L. M. DENNIS und B. J. LEMON *J. Amer. Chem. Soc.* **37**, 131 (1915).
[11] V. B. DEDOV und V. N. KOSYAKOV Proc. Int. Conf. Peaceful Uses Atomic Energy, Geneva 1955, Band 7, S. 369.
[12] L. MEITNER *Physik. Z.* **12**, 1094 (1911).
[13] F. TÖDT *Z. physik. Chem.* **113**, 329 (1924).
[14] S. COTELLE und M. HAISSINSKY *Compt. Rend.* **206**, 1644 (1938).

wurde dann in der beschriebenen Weise analysiert. Alle Präparate wurden unter gleichen geometrischen Bedingungen mit einem Endfenster-Zählrohr mit 1,9 mg/cm² Fensterdicke gemessen. Die Schichtdicke für die ^{90}Y-Fällungen betrug ungefähr 1 mg/cm², die der ^{90}Sr-Präparate 2–3 mg/cm². Die ^{90}Sr-Präparate wurden ohne Schutz gemessen, die ^{90}Y-Präparate wurden mit einer Kunststoffolie von 10 mg/cm² Dicke bedeckt. Bei der Auswertung der Aktivitätsmessungen wurde berücksichtigt, dass die Nachweiswahrscheinlichkeit für die Strahlungen der beiden Isotope unter den vorliegenden Bedingungen etwas verschieden ist.

Die pH-Messungen erfolgten mit einem pH-Messgerät mit Glaselektrode. Die pH-Werte der sauren Lösungen wurden durch Verdünnung, die der alkalischen Lösungen durch Zusatz von NH_4OH oder NaOH zu 2 N HNO_3 eingestellt.

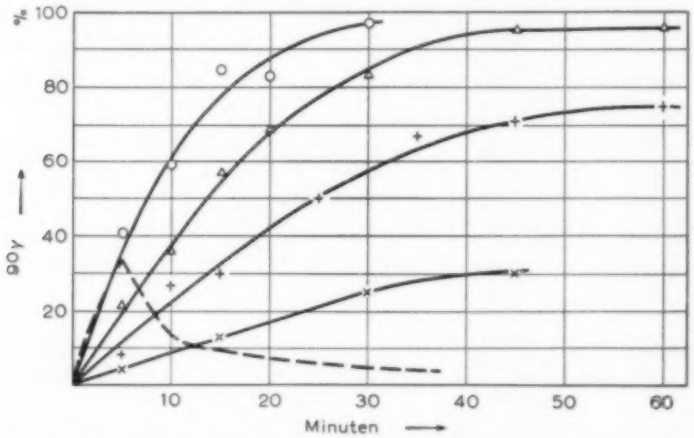

BILD 1.—Kathodische Abscheidung von ^{90}Y in Abhängigkeit von der Dauer der Elektrolyse und dem pH-Wert des Elektrolyten. Elektrolyt 30 ml HNO_3 mit 5 mg Sr^{2+} als $Sr(NO_3)_2$, Elektrodenspannung 12 Volt. —○— pH-Wert 1,51; —△— pH-Wert 2,52; —+— pH-Wert 3,68; —×— pH-Wert 5,6. Abscheidung bei 51°C (Kurve pH 1,51 bei Zimmertemperatur). — — — — anodische Abscheidung bei pH-Wert 3,68.

3. AUSARBEITUNG DES VERFAHRENS

Einfluss des pH-Wertes. Die ersten Versuche wurden gemacht mit dem Ziel, das ^{90}Y aus ammoniakalischer Lösung an der Anode abzuscheiden. Es zeigte sich jedoch bald, dass eine kathodische Abscheidung aus saurer Lösung mit höheren Ausbeuten, schneller und sauberer erfolgt. Die kathodische Abscheidung des ^{90}Y ist vom pH-Wert der Lösung abhängig. Den Einfluss des pH-Wertes und der Dauer der Elektrolyse zeigt Bild 1. Die Abscheidung beginnt bei einem pH-Wert von etwa 1,5. Mit zunehmendem pH-Wert nimmt die kathodische Abscheidung zugunsten einer anodischen ab. Letztere erreicht selbst im alkalischen Gebiet nicht mehr als etwa 60% der Gesamtmenge und schwankt stark. Die besten Ausbeuten bei der anodischen Abscheidung erreicht man bei Vermeidung jeglicher Gasentwicklung am Neutralpunkt. Im sauren Gebiet erfolgt—wie Bild 1 an einem Beispiel zeigt—die anodische Abscheidung des ^{90}Y zunächst schneller als die kathodische. Bei der Fortsetzung der Elektrolyse geht der Niederschlag an der Anode offenbar wieder in Lösung und die Abscheidung erfolgt bevorzugt an der Kathode. Die kathodische Abscheidung verläuft bei einem pH-Wert von 2,5 $\pm$ 0,3 am besten. Die Abscheidung bei pH 1,5–2,0 erfolgt zwar schneller, ist aber in der Ausbeute schwankend. Kathodische

[15] J. HARLEY und N. HALLDEN *Nucleonics* **13**, 32 (1955).

Abscheidungen des ^{90}Y sind auch möglich aus HCl bei pH 2,5 und aus Essigsäure.

Fremdionen. Für die Reinheit des abgeschiedenen ^{90}Y ist der Zusatz von Fremdionen zum Elektrolyten, hier $Sr(NO_3)_2$ oder NH_4NO_3, günstig (vgl. Abschnitt 4). Die Abscheidung wird dadurch jedoch verzögert. Das zeigt Bild 2, wo die Ausbeuten

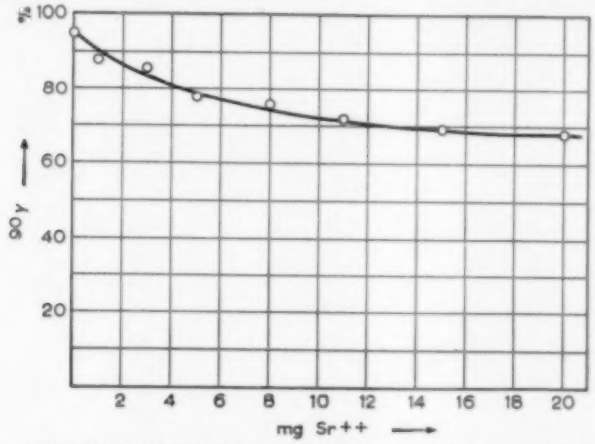

BILD 2.—Abhängigkeit der kathodischen Abscheidung von ^{90}Y vom Gehalt des Elektrolyten an Sr^{2+}. Elektrolyt 30 ml HNO_3 mit dem pH-Wert 2,30; Temperatur 51°C; Elektrodenspannung 12 Volt; Dauer der Elektrolysen 30 min. Das Sr^{2+} wurde als $Sr(NO_3)_2$ zugegeben.

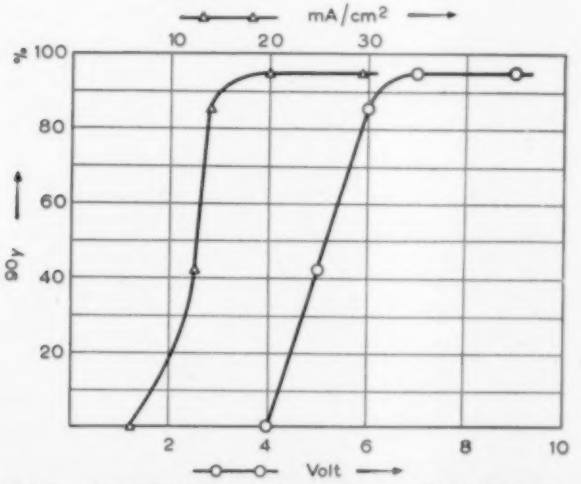

BILD 3.—Einfluss der Stromdichte und der Spannung auf die kathodische Abscheidung des ^{90}Y. —○— Spannung; —△— Stromdichte. Elektrolyt 30 ml HNO_3, pH-Wert 2,54; mit 5 mg Sr^{2+} als $Sr(NO_3)_2$. Temperatur 56°C, Dauer der Elektrolysen 60 min.

bei gleicher Dauer der Elektrolyse gegen den Gehalt an Sr^{2+} im Elektrolyten aufgetragen sind. Ähnlich verzögernd wirkt $NaNO_3$.

Stromdichte, Spannung. Stromdichte und Spannung sind für die kathodische Abscheidung des ^{90}Y von Bedeutung. Die Ausbeuten in Abhängigkeit von Spannung und Stromdichte sind in Bild 3 aufgetragen. Die kathodische Abscheidung beginnt,

sobald die Gasentwicklung einsetzt und der Stromdurchgang wesentlich wird. Die anodische Abscheidung dagegen erfolgt wohl durch Elektrophorese. Sie setzt schon vor Beginn der Gasentwicklung ein.

Temperatur. Den Temperatureinfluss auf die kathodische Abscheidung des ^{90}Y zeigt Bild 4. Die Abscheidung erfolgt um so schneller, je höher die Temperatur ist.

Einfluss von H_2O_2. Der Einfluss von H_2O_2 auf die Abscheidung wurde geprüft, da bei der Verarbeitung starker Präparate mit der Bildung von H_2O_2 durch Strahlenwirkung auf Wasser zu rechnen ist (Tabelle 1).

Konstanz des pH-Wertes; Konzentration an $^{90}Y/^{90}Sr$. Für die Abscheidung

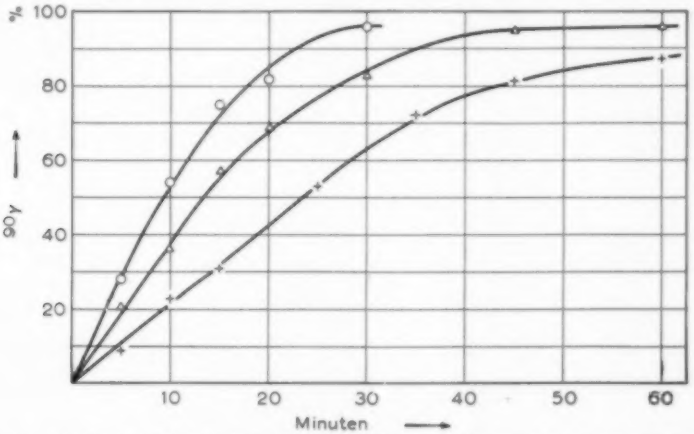

BILD 4.—Abhängigkeit der kathodischen Abscheidung von ^{90}Y von der Zeit bei verschiedenen Temperaturen.
—○—Temperatur 75°C; —△—Temperatur 51°C; —+—Temperatur 26°C. Elektrolyt 30 ml HNO_3, pH-Wert 2,52, mit 5 mg Sr^{2+} als $Sr(NO_3)_2$; Elektrodenspannung 12 Volt.

wesentlich ist die Konstanz des pH-Wertes der Lösung. Sind die verwendeten Lösungen, einschliesslich der $^{90}Y/^{90}Sr$-Lösung, frei von wägbaren Verunreinigungen, so bleibt der pH-Wert bei mehrere Stunden dauernder Elektrolyse konstant. Sind dagegen Verunreinigungen vorhanden, wie z.B. Fe, so zeigt sich an der Kathode eine mehr oder weniger starke Schwärzung, wodurch die Zersetzung der HNO_3 stark beschleunigt wird. Infolge der dadurch bedingten Verschiebung des pH-Wertes

TABELLE 1

Nr.	% H_2O_2 im Elektrolyt.	Gegeben ^{90}Y (Imp./min)	Ausbeute an ^{90}Y (in %)
1	0	$1{,}05 \cdot 10^6$	68
2	0,5	$1{,}05 \cdot 10^6$	67
3	1,0	$1{,}05 \cdot 10^6$	69
4	2,0	$1{,}05 \cdot 10^6$	32
5	3,0	$1{,}05 \cdot 10^6$	25

Einfluss von H_2O_2 auf die kathodische Abscheidung des ^{90}Y. Elektrolyt 30 ml HNO_3, pH-Wert 2,1, 15 mg Sr^{2+}, Temperatur 51°C. 12 Volt Elektrolysespannung.

wird die kathodische Abscheidung des ^{90}Y sehr beeinflusst. Stammen diese Verunreinigungen aus der aktiven Lösung, so kann man sie durch mehrmalige Elektrolyse entfernen, wobei man nach jeder Elektrolyse den pH-Wert der Lösung neu einstellt. Bei sauberen Reagenzien und Lösungen bleibt die Kathode vollkommen blank.

Die Konzentration des Elektrolyten an $^{90}Y/^{90}Sr$ ist für die Abscheidung ohne Bedeutung. Es wurden aus 30 ml von 0,35 μC bis zu 20 mC ^{90}Y ohne Störungen abgeschieden.

4. REINHEIT DES ^{90}Y

Die nachfolgenden Versuche sind nach dem in Abschnitt 5 beschriebenen Verfahren durchgeführt worden. Tabelle 2 zeigt zunächst, dass ein Zusatz von 5 mg Sr^{2+} die Abscheidung des ^{90}Sr auf etwa die Hälfte vermindert. Das gilt für die kathodische Abscheidung. Die Verunreinigung an ^{90}Sr bei anodischer Abscheidung des ^{90}Y und die bei kathodischer in Gegenwart von H_2O_2 nach einmaliger Elektrolyse zeigen einige Werte der Tabelle 3a und 3b. Die anodische Abscheidung ergibt demnach nicht nur geringere Ausbeuten (vgl. Abschnitt 3), sondern

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TABELLE 2

Nr.	Zusatz an Sr^{2+} bei der Elektrolyse (in mg)	Abgeschieden		^{90}Sr im ^{90}Y (in %)
		^{90}Y (Imp./min)	^{90}Sr (Imp./min)	
1	0,1	38 000	258	0,7
2	0,1	36 300	344	1,0
3	0,1	31 500	337	1,1
4	0,1	35 000	251	0,7
5	5,0	948 000	4 810	0,5
6	5,0	1007 000	5 540	0,6
7	5,0	1040 000	4 050	0,4

Gehalt des ^{90}Y an ^{90}Sr nach einmaliger kathodischer Abscheidung.

TABELLE 3

Nr.	Zusatz an Sr^{2+} bei der Elektrolyse (in mg)	Abgeschieden		^{90}Sr im ^{90}Y (in %)
		^{90}Y (Imp./min)	^{90}Sr (Imp./min)	
1	0,1	$239 \cdot 10^3$	4 850	2,0
(a.) 2	0,1	$247 \cdot 10^3$	6 300	2,6
3	0,1	$165 \cdot 10^3$	10 650	6,5
4	5,0	$685 \cdot 10^3$	17 000	2,5
(b.) 5	5,0	$850 \cdot 10^3$	24 000	2,8
6	5,0	$900 \cdot 10^3$	23 000	2,6

Gehalt des ^{90}Y an ^{90}Sr (a.) nach einmaliger anodischer Abscheidung, (b.) bei kathodischer Abscheidung in Gegenwart von H_2O_2 im Elektrolyten.

auch grössere Gehalte an ^{90}Sr. Bei Gegenwart von H_2O_2 findet man nach der Elektrolyse einen weissen Überzug an der Kathode. Die ^{90}Sr-Gehalte übersteigen die in H_2O_2-freien Lösungen beobachteten bei weitem.

Durch Wiederholung der Elektrolyse wird der ^{90}Sr-Gehalt des ^{90}Y weiter vermindert. Aus den Werten der Tabelle 4 ist die günstige Wirkung des Zusatzes von Strontiumnitrat und Ammoniumnitrat ersichtlich. Der Fortschritt der weiteren Reinigung ist aus den Tabellen 5 und 6 zu entnehmen. Tabelle 5 gilt für dreimalige Elektrolyse, Tabelle 6 für viermalige. Es wurden jeweils bei der ersten Elektrolyse 5,0 mg Sr^{2+} zugesetzt, bei den weiteren je 15 mg.

TABELLE 4

Nr.	Zusatz an Sr^{2+} bei 1.(a) und 2.(b) Elektrolyse (in mg) a	b	Abgeschieden ^{90}Y (Imp./min)	^{90}Sr (Imp./min)	^{90}Sr im ^{90}Y (in %)
1	5,0	15,0	$90 \cdot 10^4$	160	$2 \cdot 10^{-2}$
2	5,0	15,0	$75 \cdot 10^4$	25	$3 \cdot 10^{-3}$
3	5,0	15,0	$85 \cdot 10^4$	15	$2 \cdot 10^{-3}$
4	1,5	12,5	$171 \cdot 10^4$	74	$4 \cdot 10^{-3}$
5	—	—	$82{,}5 \cdot 10^4$	200	$2 \cdot 10^{-2}$
6	—	—	$62{,}5 \cdot 10^4$	170	$3 \cdot 10^{-2}$
7	—	—	$100 \cdot 10^4$	600	$6 \cdot 10^{-2}$
	a	b NH_4NO_3 in mg			
8	5,0	20,0	$90 \cdot 10^4$	40	$5 \cdot 10^{-3}$
9	5,0	20,0	$95 \cdot 10^4$	15	$2 \cdot 10^{-3}$
10	5,0	20,0	$99 \cdot 10^4$	15	$2 \cdot 10^{-3}$

^{90}Sr-Gehalt des ^{90}Y nach zweimaliger kathodischer Abscheidung.

TABELLE 5

Nr.	Abgeschieden ^{90}Y (Imp./min)	^{90}Sr (Imp./min)	^{90}Sr im ^{90}Y (in %)
1	$86 \cdot 10^6$	45	$5 \cdot 10^{-5}$
2	$80 \cdot 10^6$	53	$7 \cdot 10^{-5}$
3	$159 \cdot 10^6$	56	$4 \cdot 10^{-5}$
4	$97 \cdot 10^6$	514	$5 \cdot 10^{-4}$
5	$129 \cdot 10^6$	191	$1{,}5 \cdot 10^{-4}$
6	$58 \cdot 10^6$	231	$4 \cdot 10^{-4}$
7	$87 \cdot 10^6$	102	$1 \cdot 10^{-4}$
8	$104 \cdot 10^6$	405	$4 \cdot 10^{-4}$

^{90}Sr-Gehalt des ^{90}Y nach dreimaliger kathodischer Abscheidung.

TABELLE 6

Nr.	Abgeschieden		^{90}Sr im ^{90}Y (in %)
	^{90}Y (Imp./min)	^{90}Sr (Imp./min)	
1	$81 \cdot 10^6$	<5	$<6 \cdot 10^{-6}$
2	$77 \cdot 10^6$	16	$2 \cdot 10^{-5}$
3	$143 \cdot 10^6$	<5	$<4 \cdot 10^{-6}$
4	$93 \cdot 10^6$	342	$4 \cdot 10^{-4}$
5	$122 \cdot 10^6$	29	$2{,}5 \cdot 10^{-5}$
6	$54 \cdot 10^6$	79	$1{,}5 \cdot 10^{-4}$
7	$83 \cdot 10^6$	14	$2 \cdot 10^{-5}$
8	$100 \cdot 10^6$	9	$1 \cdot 10^{-5}$

^{90}Sr-Gehalt des ^{90}Y nach viermaliger kathodischer Abscheidung.

Lässt man nach viermaliger Elektrolyse das abgeschiedene ^{90}Y zerfallen und analysiert das ^{90}Sr-Präparat nach HARLEY-HALLDEN, so findet man neben dem ^{90}Sr eine schwache Fremdaktivität, die noch nicht näher identifiziert werden konnte. Das Reinigungsverfahren ist also begrenzt durch Fremdaktivitäten, die in dem ^{90}Y/^{90}Sr vorhanden sind und unter den gleichen Bedingungen abgeschieden werden. Aus den angeführten Werten folgt, dass das ^{90}Y bis auf etwa 10^{-4} bis 10^{-5}% ^{90}Sr zu reinigen ist. Die Ausbeuten nach viermaliger Elektrolyse erreichen 70 bis 80% der Ausgangsmenge. Noch geringere Gehalte an ^{90}Sr lassen sich mit dem Verfahren zweifellos erreichen, allerdings sinkt die Ausbeute gleichzeitig weiter ab.

5. ARBEITSVORSCHRIFT

Aus den vorhergehenden Abschnitten ergibt sich folgende Arbeitsvorschrift:

Eine ^{90}Y/^{90}Sr-Lösung wird vorsichtig eingedampft, mit einigen Tropfen konzentrierter HNO_3 abgeraucht und mit HNO_3 vom pH-Wert 2,5 $\pm$ 0,3 aufgenommen. Dann wird zum Sieden erhitzt und anschliessend die Temperatur auf etwa 50 °C gehalten. Der Zusatz von *ca.* 10 mg $Sr(NO_3)_2$ oder 20 mg NH_4NO_3 vermindert den ^{90}Sr-Gehalt der ^{90}Y-Abscheidung. Aus dieser Lösung wird jetzt das ^{90}Y kathodisch in 45 bis 60 Minuten mit 12 Volt Spannung an Platinelektroden abgeschieden. Gerührt wird mit der Kathode oder elektromagnetisch. Man achtet darauf, dass die Stromdichte etwa 20 mA/cm² an der Kathode erreicht.

Nach Beendigung der Abscheidung wird die Kathode unter Strom aus der Lösung herausgezogen und mit Alkohol oder Aceton gespült. Die weitere Reinigung des abgeschiedenen ^{90}Y geschieht so: Die Kathode mit dem ^{90}Y aus der 1. Elektrolyse wird in ein neues Elektrolysebad getaucht und dort als Anode geschaltet. Eine neue Kathode wird eingesetzt. Der Elektrolyt besteht wie zuvor aus 30 ml HNO_3, pH-Wert 2,5, sowie 20 bis 30 mg inaktivem $Sr(NO_3)_2$ oder 20 mg NH_4NO_3. Dann wird wieder mit 12 Volt Spannung elektrolysiert, wobei das ^{90}Y von der Anode an die Kathode wandert. Diese Reinigung wird so lange wiederholt, bis der erwünschte Reinheitsgrad erreicht ist. Nach insgesamt drei bis vier Elektrolysen beträgt der Gehalt des ^{90}Y an ^{90}Sr weniger als 10^{-4}%.

Die Ausgangslösung steht für weitere Abtrennungen unverändert zur Verfügung.

6. DISKUSSION

Eine eingehende Diskussion des Mechanismus der kathodischen wie anodischen Abscheidung von ^{90}Y in unwägbarer Menge ist mit dem vorliegenden Material nicht möglich. Hier müssen weitere Untersuchungen Klarheit bringen. Es lassen

sich lediglich einige Vergleiche zu anderen Untersuchungen ziehen. So stimmen die von DEDOV und KOSYAKOV[11] gemessenen Abscheidungsgeschwindigkeiten unwägbarer Mengen Am^{3+} und Cm^{3+} an der Kathode etwa mit den von uns für Y^{3+} unter gleichen Bedingungen (pH-Wert 2,5, HNO_3-saure Lösung) gefundenen überein. Sicherlich lassen sich einige der von diesen Autoren zur Erklärung der Kinetik durchgeführten Betrachtungen auch auf unseren Fall übertragen. Wesentliche Unterschiede werden jedoch in der pH-Abhängigkeit der Abscheidungsgeschwindigkeit und der maximal an der Kathode abgeschiedenen Menge beobachtet. Beim Y^{3+} erfolgt die Abscheidung bei einem pH-Wert von 1,5–2,5 am schnellsten und mit fast quantitativer Ausbeute, Geschwindigkeit und Ausbeute sinken bei höheren pH-Werten stark ab. (Bild 1). Beim Am^{3+} wird das Maximum der Abscheidungsgeschwindigkeit und Ausbeute erst beim pH-Wert $\sim$4 erreicht, scheint aber bei der Erhöhung des pH-Wertes ebenfalls abzusinken.

Man wird weiter annehmen können, dass die Hydrolyse des Y^{3+}, die bei der Elektrolyse wägbarer Mengen in wässriger Lösung entscheidend ist[10,11] und zur kathodischen Abscheidung von Hydroxyden führt, auch bei unwägbaren Mengen eine Rolle spielt. Dafür spricht, dass unterhalb vom pH-Wert $\sim$ 1 keine Abscheidung beobachtet wird. Es scheint also auch hier eine Hydrolyse in unmittelbarer Nähe der Kathode, bedingt durch die Verarmung an H^+-Ionen, der Abscheidung vorauszugehen. Einige orientierende Messungen über den Einfluss des pH-Wertes auf die anodische Abscheidung zeigen, dass diese etwa vom pH-Wert 3,5 an merklich wird, bei pH 5–7 ihren grössten Wert erreicht und im alkalischen Gebiet wieder zurückgeht Diese pH-Abhängigkeit stimmt gut überein mit der pH-Abhängigkeit der Radiokolloidbildung von unwägbarem Y^{3+}, die SCHWEITZER, STEIN, und JACKSON[4] untersucht haben. Radiokolloides Y^{3+} scheint also zur Anode zu wandern und zwar auch dann, wenn kein Strom fliesst. Zugleich wird durch die Radiokolloidbildung die kathodische Abscheidung vermindert. Die Wanderung des Yttriums zur Kathode dürfte demnach als Y^{3+} erfolgen.

Die Abscheidung des Sr^{2+} an der Kathode wird zumindest teilweise als Karbonat erfolgen. Bei einigen Versuchen haben wir die Abscheidung sichtbarer Mengen $SrCO_3$ an der Eintauchstelle der Elektrode in die Lösung beobachtet. VON BAEYER, HAHN, und MEITNER[16,13] konnten Radiumisotope in Gegenwart sehr kleiner Mengen Ba^{2+} aus schwach sauren Lösungen, in die CO_2 eingeleitet wurde, mit guter Ausbeute kathodisch abscheiden. Herrn Dr. med. K. E. SCHEER, Heidelberg, verdanken wir die Anregung dieser Arbeit und das verwendete $^{90}Sr/^{90}Y$. Das bei der Untersuchung benutzte Strahlungsmessgerät wurde uns von der *Deutsche Forschungsgemeinschaft* zur Verfügung gestellt, wofür wir herzlich danken möchten.

[16] O. v. BAEYER, O. HAHN, und L. MEITNER *Physik. Z.* **16**, 6 (1915).

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THE SZILARD-CHALMERS REACTION IN POTASSIUM COBALTICYANIDE*

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Abstract—Dissolution of neutron-irradiated potassium cobalticyanide in water produces cobaltous ion and anionic species having six, five, and four cyanides per cobalt. The distribution of active cobalt among these ions as a function of pH and thermal annealing has been investigated, and the data have beeen interpreted in terms of recoil fragments, also having six, five and four cyanides per cobalt, in the crystal following irradiation. We have interpreted the observed re-formation of $Co(CN)_6^{---}$ during thermal annealing as due to a recombination of cyanide with tetra- and pentacyano fragments.

THE complex six-co-ordinate compounds of cobalt-III have for a long time interested chemists, and an enormous number of them have been synthesized and investigated. A few studies have also been made of the chemistry of cobalt recoil atoms in selected cobalt complexes.[1–4] For this study, potassium cobalticyanide was chosen. It had not been examined before, was readily available, and could be easily recrystallized and dried to the anhydrous condition. In addition, cobalticyanide ion is stable in the crystal and in solution over a wide range of pH, and may be readily separated from cobaltous ion. Cobaltous ion and cobalticyanide do not exchange in solution nor in crystalline cobaltous cobalticyanide.[5]

Finally, it was felt that a detailed study of the hot-atom chemistry of a negative complex ion of cobalt-III might afford an interesting comparison with that already carried out by ZUBER[1] on the positive complex, cobaltic trisethylenediamine.

EXPERIMENTAL

Materials. Potassium cobalticyanide was obtained from City Chemical Corporation, New York City, and was recrystallized from water and oven-dried before use. The dry material, although not hygroscopic, was stored in a desiccator.

Alpha-nitroso beta-naphthol was supplied by Eastman Kodak and was used without purification. All other chemicals were Reagent grade.

For the electrophoresis experiments, single thicknesses of Whatman No. 3 paper were taken.

Bombardments. Bombardments were made with neutrons in the Brookhaven reactor. Three types of bombardment were employed: (i) 1-or 3-min bombardments in the pneumatic tube, with the salt either at room or dry-ice temperature. The flux was about $1{\cdot}2 \times 10^{12}$ n/cm² sec. (ii) 30-min bombardments at dry-ice temperature. (iii) 30-min bombardments in the water-cooled hole. The flux was about the same as in (i) and (ii), but the temperature was maintained at 25–30°C. Samples

* Some preliminary results of this research were presented at the Symposium on Nuclear and Radiochemistry, McGill University, Montreal, Canada, 7–9 September 1955.

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[1] A. ZUBER Dissertation, Faculty of Pure Science, Columbia University, New York (1954).
[2] P. SÜE and G. KAYAS *J. Chim. Phys.* **45**, 188 (1948).
[3] S. CHATTERJEE and P. RÂY *Trans. Bose Research Inst. Calcutta* **13**, 43 (1937-8) [*C.A.* **35**, 688 (1941)].
[4] J. STEIGMAN *Phys. Rev.* **59**, 498 (1941).
[5] J. F. FLAGG *J. Amer. Chem. Soc.* **63**, 557 (1941).

from (ii) and (iii) were used in the electrophoresis studies, since higher specific activities were necessary. In the 1-min bombardments the samples were in plastic ampoules, while for the longer bombardments they were sealed in quartz tubes. All bombardments were made in the presence of air. All samples were permitted to stand for at least 1 week before measurement to allow the ^{42}K activity to decay, and then contained only ^{60}Co activity.

Separation procedure. For most of the retention measurements, the following separation procedure was used: 5 to 30 mg of the irradiated salt was dissolved in 30 ml of a saturated aqueous α-nitroso β-naphthol solution which had been buffered with acetic acid and sodium acetate to pH 5·4. The solution was then boiled for 5 min, cooled, and extracted, first with 30 ml and then with 15 ml of benzene. The extracts were combined and diluted with benzene to 50 ml in a volumetric flask, while the extracted solution was diluted to 50 ml with water. The two solutions were counted in glass cells with a scintillation counter, and the "retention" calculated (after corrections for background) as

$$R\,(\%) = \frac{\text{counting rate of aqueous phase}}{\text{sum of counting rates of aqueous and organic phases}} \times 100.$$

Duplicate or quadruplicate samples were taken and the results were usually reproducible to $\pm 1\%$ in the retention for a set of four samples. Experiments with tracer cobaltous ion showed that extraction of the cobalt complex into benzene was more than 99·5% complete. It was also demonstrated that cobalticyanide does not extract.

Electrophoresis procedure. For the electrophoresis studies of the species formed in recoil, samples of the longer-irradiated salt (see Bombardments (ii) and (iii) above) were dissolved in various media at a concentration of about 10 mg/ml. Portions of 3 to 10 λ were then pipetted and placed at a zero-line on the electrophoresis papers. The latter were strips of Whatman No. 3 paper cut 3·8 cm wide and about 55 cm long; the last 5 cm on either end had been trimmed to form "tails" roughly 2 mm wide which dipped into electrolyte tanks. Before use these strips were soaked in the electrolyte solution (usually pH-5·4 acetate buffer) and blotted firmly between sheets of blotter paper or "Kimpak." After the solution to be examined had been placed on the blotted strip at the zero-line, the strip was clamped between two glass plates 45 cm square whose surfaces touching the paper had been treated with "Drifilm." Provision was made for cooling the upper plate with water. Contact was then made, through graphite electrodes dipping in the electrolyte tanks, with a d.c. voltage source* and potentials of the order of 450–700 volts were applied (10 to 16 volts/cm gradient). After 2–5 hours the voltage was interrupted, the apparatus disassembled, and the paper dried in air. When dry the paper was cut transversely into 1-cm wide strips; these were folded in a standard way, mounted on cards and scintillation-counted. In several cases, the strips after counting were individually analysed for cobalt by the nitroso-R-salt method.[6]

EXPERIMENTAL RESULTS

Verification of non-exchange of cobaltous ions and cobalticyanide. It had been reported by FLAGG[5] that cobalt-II and cobalticyanide do not exchange in solution nor in the crystalline compound cobaltous cobalticyanide. It was thought desirable to check this observation and it was verified that there is no exchange in a half-hour at room temperature in either pH-5·4 buffer or 0·05 F perchloric acid. The concentrations were about 0·001 F in cobaltous ion and cobalticyanide. In the latter case, cobaltous cobalticyanide gradually precipitated; it could be dissolved with concentrated ammonia and the solution was then analysed by separating the cobaltic hexamine and cobalticyanide ions electrophoretically. The results (no exchange observed) thus also confirm FLAGG's observation on the solid compound, cobaltous cobalticyanide.

* New Jersey Electronics model S-300-c.

[6] E. B. SANDELL *Colorimetric Determination of Traces of Metals* p. 277. Interscience Publishers, New York (1950) The procedure was modified by the substitution of a perchloric acid fuming for evaporation with nitric acid.

Effect of temperature at bombardment site on retention. The effect of the temperature of bombardment and of storage of the irradiated salt was investigated. It was found (Table 1) that bombardment at dry-ice temperature resulted in lower retentions than bombardment for the same length of time at room temperature, subsequent storage being the same. It was also found that storage at ice-box temperature (10°C) produced a partial annealing of the recoil atoms (increase in retention) in a period of 1 week, and that even at dry-ice storage temperature some annealing occurred after 4 weeks. Finally, it was observed many times (some typical results are reported in Table 1) that different lots of crystals produced somewhat different initial retentions. The cause of these differences, whether due to impurities, traces of moisture in the preparations, or difference in radiation dosage in the reactor, was not discovered.

TABLE 1.—EFFECT OF TEMPERATURES OF IRRADIATION AND STORAGE UPON RETENTION

Irradiation temperature	Length of irradiation	Storage temperature	Storage time	Retention[a] (%)
Room	3 min	10°C	1 week	48·0
Room	3 min	dry ice	1 week	41·1
Dry ice	3 min	dry ice	1 week	36·2, 34·3, 34·6
Dry ice	1 min	dry ice	1 week	35·8, 34·9
Dry ice	1 min	dry ice	1 week	40·6, 41·9[b]
Dry ice	3 min	dry ice	4 weeks	37·8[c]

[a] Each figure represents a single sample (i.e. bombardment) of crystals from the same preparation (except [b]) and is an average of two or more determinations. Errors are ±1 in retention percentages.
[b] A different lot of crystals (different preparation).
[c] This is a sample which had a retention of 34·3% after 1-week storage.

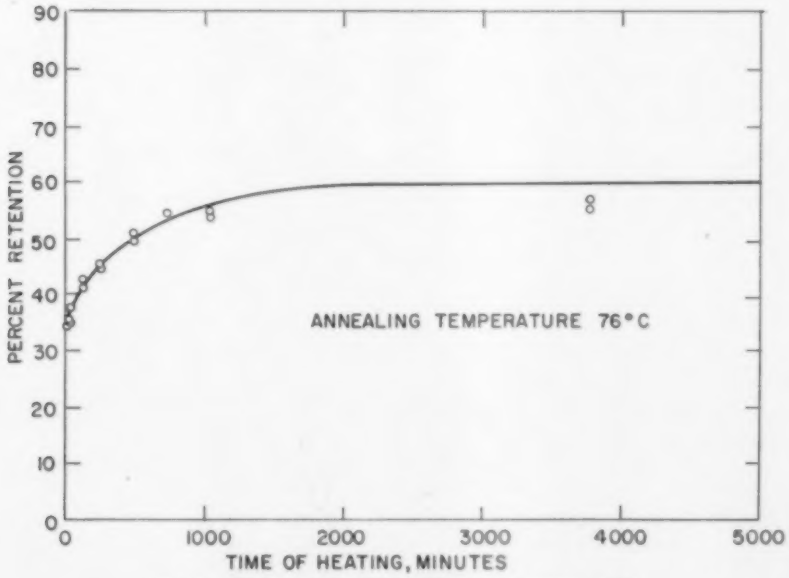

FIG. 1.—Effect of thermal annealing upon retention, 76°C.

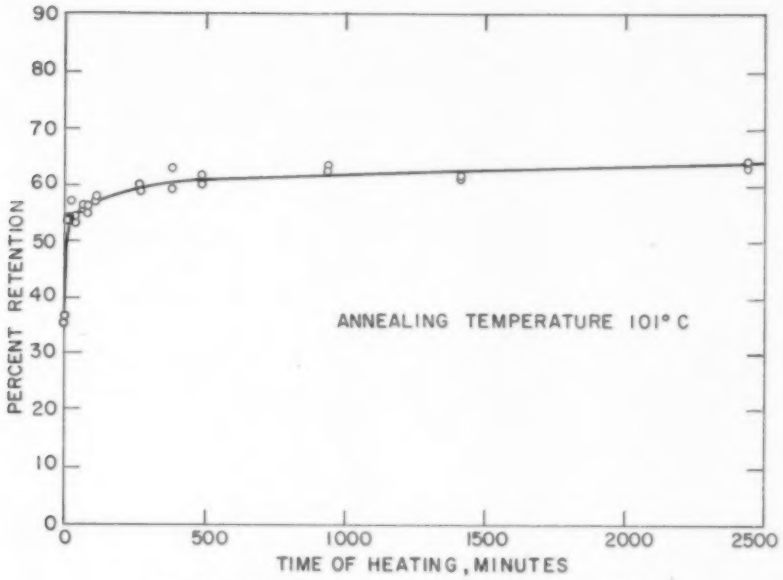

FIG. 2.—Effect of thermal annealing upon retention, 101°C

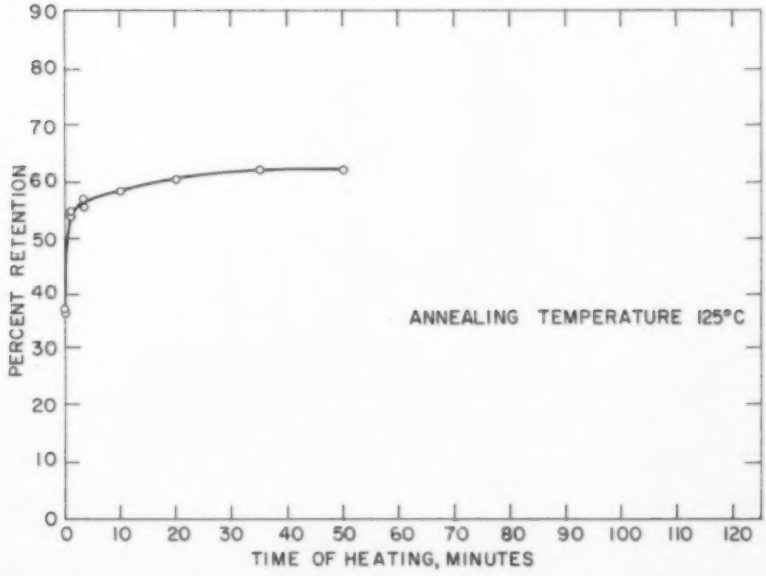

FIG. 3.—Effect of thermal annealing upon retention, 125°C

However, all annealing studies were done with material having the lowest initial retention (about 35%).

Effect of heating. Annealing behaviour. In the light of these results, the following procedure was adopted. After bombardment at dry-ice temperature for 1 min. samples were stored under dry ice for a week to permit ^{42}K activity to decay. Samples of the irradiated salt were then heated for measured periods of time at the specified temperature and the retention determined. Results of these annealing experiments are plotted in Figs. 1, 2, and 3, the temperature being 76°, 101°, and 125°C.

It is interesting that these three curves appear to converge, after long heating times, at a value of $R \simeq 63\%$. In this regard, potassium cobalticyanide is markedly different from potassium chromate, where the plateau value of the retention after long heating times is a function of the temperature.[7]

Effect of radiation on the retention. A partially-annealed sample of irradiated potassium cobalticyanide was exposed to the radiation of a cobalt-60 source at room temperature. The retention increased with radiation dose, indicating, in a qualitative way, the presence of a radiation-induced anneal of the type observed in a number of other systems.[8] Upon gamma-irradiation, the clear pale-yellow crystals took on a violet coloration which persisted for weeks following the exposure. The result of a similar experiment, in which the gamma-irradiated sample was subjected to electrophoresis, is presented in Table 2.

TABLE 2.—PERCENTAGE DISTRIBUTION OF IONIC SPECIES IN IRRADIATED $K_3Co(CN)_6$ DISSOLVED IN pH 5·4 BUFFER AS A FUNCTION OF STATE OF ANNEAL

State of anneal	$Co(CN)_6^{---}$	$Co(CN)_5H_2O^{--}$	$Co(CN)_4(H_2O)_2^{-}$	$Co(CN)_4(NH_3)_2^{-}$	Co^{++}	Unaccounted for
Freshly bombarded	19	16	6	—	55	4
Two months storage at −78°C	26	16	3	—	52	3
Four months storage at −78°C	31	14	3	—	50	2
After storage at room temperature for 3 months	44	14	3	—	38	1
	42	16	3		38	1
	43	11	4		35	7
Fresh sample annealed 1 hr at 100°C	42	13	3	—	38	4
Annealed 3·5 hr at 100°C	44	15	3	—	36	2
Annealed 2 hr at 125°C	50	13	3	—	30	4
Annealed by exposure to cobalt-60 gamma rays, $1·7 \times 10^8$ roentgens at room temperature	60	14	4	—	17	5

[7] A. G. MADDOCK and M. M. DE MAINE *Canad. J. Chem.* **34**, 275 (1956).

[8] R. WILLIAMS *J. Phys. Colloid Chem.* **52**, 603 (1948); J. GREEN, G. HARBOTTLE, and A. G. MADDOCK *Trans. Faraday Soc.* **49**, 1413 (1953); G. HARBOTTLE *J. Chem. Phys.* **22**, 1083 (1954); R. E. CLEARY, W. HAMILL, and R. WILLIAMS *J. Amer. Chem. Soc.* **74**, 4675 (1952); G. E. BOYD, J. COBBLE, and S. WEXLER *J. Amer. Chem. Soc.* **74**, 237 (1952); J. COBBLE and G. E. BOYD *J. Amer. Chem. Soc.* **74**, 1282 (1952).

Attempted identification (by electrophoresis) of fragments formed in recoil. The application of the technique of paper electrophoresis (which we also call "ionography") to hot-atom studies was suggested by CROATTO, GIACOMELLO, and MADDOCK.[9]

Irradiated potassium cobalticyanide was dissolved in acetate buffer (pH 5·4) and the solution examined ionographically. The voltage was applied in such a way that negative ions moved to the right, positive ions to the left of the starting line, which is indicated in the histograms by a dotted line. In a large number of experiments with different lots of crystals, histograms similar to Fig. 4 (radioactivity determined on a scintillation counter vs. distance along the paper) were invariably obtained.

The peak farthest to the right was identified as the parent ion (cobalticyanide) in two ways: (i) its rate of motion was identical with that of a known sample of

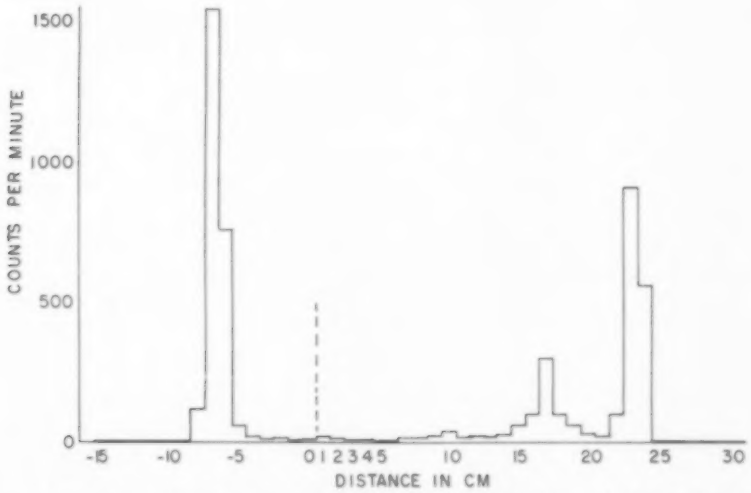

FIG. 4.—Electrophoresis pattern of irradiated potassium cobalticyanide dissolved in pH 5·4 buffer. Radioactivity versus distance. Dotted line indicates starting position, anions move right.

cobalticyanide which had been synthesized with labelled cobalt-60 by the method of BIGELOW,[10] and (ii) a strip-by-strip analysis of the paper for cobalt (by the nitroso-R-salt method) revealed that macroscopic quantities of cobalt were present only in the peak farthest to the right, and in amounts proportional to the activity of the cobalt-60 in the fractions composing that peak.

In similar fashion, using labelled cobaltous ion, the peak to the left of the starting line was identified as Co^{++}.

The third peak, an anion moving more slowly than cobalticyanide, was designated the *X* peak for convenience and was observed every time irradiated potassium cobalticyanide was dissolved in aqueous solutions. Likewise, the fourth peak, also an anion but moving more slowly than the *X* peak, and much smaller than it, was observed nearly every time. This fourth peak was designated the *A* peak.

[9] U. CROATTO, G. GIACOMELLO, and A. G. MADDOCK *Ric. Sci.* **21**, 1788 (1951).
[10] *Inorganic Syntheses* Vol. II, p. 225. McGraw-Hill, N.Y. (1946).

Since the radioactivity of the *X* peak amounted to roughly 15% of the total, it was thought desirable to find whether, under the conditions of analysis employed in the retention studies (see "Separation procedure" above), the *X*-peak activity ultimately entered the "cobaltous" or "cobalticyanide" fraction. To determine this, a sample of irradiated salt was dissolved in the α-nitroso β-naphthol reagent and boiled for 5 min. The resulting solution was ionographed and the histogram

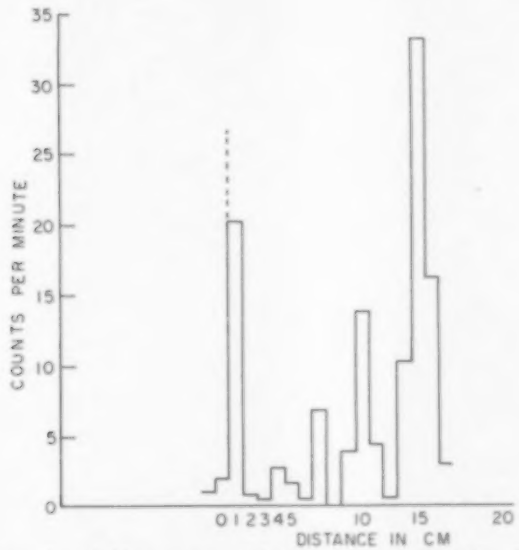

FIG. 5.—Electrophoresis histogram: crystals dissolved in α-nitroso β-naphthol reagent.

of Fig. 5 was obtained. As expected, the cobalt α-nitroso β-naphthol complex, being neutral, remained at the starting line, but the *X* peak still existed as an anionic species. There was some indication, although counting statistics were poor, that the *A* peak also remained. Since the extractant was benzene, it seems unlikely that the *X* and *A* material would extract, and therefore these activities must be considered as remaining with the "cobalticyanide" fraction. This conclusion was borne out by a comparison of the results of electrophoresis with solvent extraction experiments on both crystals bombarded at dry-ice temperature and the same crystals when annealed. Agreement between the two methods was obtained for the "retention" in both lots of crystals only if the *X* peak, at least, was included in the "cobalticyanide" fraction.

It was guessed that the *X* and *A* peaks might actually be pentacyano monaquo and tetracyano diaquo cobaltate III ions respectively. These were chosen for the following reasons: (i) both *X* and *A* are anions containing cobalt; (ii) they are probably closely related to $Co(CN)_6^{=}$, as they arise from species formed in the crystal by recoil; (iii) if the ionic radii of all three were similar, their rates of motion should increase with increasing charge in the sequence $Co(CN)_4(H_2O)_2^-$, $Co(CN)_5H_2O^{=}$, and $Co(CN)_6^{=}$. Both $Co(CN)_4(H_2O)_2^-$ and $Co(CN)_5H_2O^{=}$ are

reported in the literature[11–16] to be reasonably stable entities. Species such as $Co(CN)_3$ or $Co(CN)_3(H_2O)_x$, $Co(CN)_2^+$, etc., could be excluded on the basis of ionic charge, while species such as $Co(CN)_5OH^{=}$ and $Co(CN)_4(OH)_2^{=}$[16] could not of course be excluded *a priori*. Species in which the cobalt was divalent would probably be converted to trivalent species by air oxidation.

A synthesis of the compound potassium pentacyano monaquo cobaltate-III by the method of RÂY and DUTT[11] was first attempted, and the material thus prepared was examined by the method of electrophoresis. Unfortunately, the product (which can be obtained only in solution) appeared to be a mixture. The major component, however, moved at a rate identical with that of the *X* peak.

The work of ADAMSON[14] and of HUME and KOLTHOFF[15] indicate that when cyanide ion is added to cobaltous ion in solution, the following sequence of reactions occurs:

$$Co^{++} + 2CN^- \longrightarrow Co(CN)_2 \text{ (brown precipitate)} \quad (1)$$

$$Co(CN)_2 + 3CN^- \longrightarrow Co(CN)_5^{=} \quad (2)$$

$$H_2O + Co(CN)_5^{=} \xrightarrow[\text{oxidation}]{} Co(CN)_5H_2O^- \quad (3)$$

The oxidation in reaction (3) may be carried out by air or other oxidizing agents such as ferricyanide. The species $Co(CN)_5H_2O^-$ is apparently quite stable and does not go to $Co(CN)_6^{=}$ unless a large excess of cyanide is present.

This extremely simple synthesis of $Co(CN)_5H_2O^-$ was carried out using labelled cobalt in the proportion of one cobalt to about six cyanides. Electrophoretic examination of the product yielded the histogram given in Fig. 6, in which it is seen that there is a small peak farthest right ($Co(CN)_6^{=}$ formed in small yield) and to the left of this a large main peak. Further experiments with bombarded potassium cobalticyanide showed that this main peak in the Adamson preparation did in fact move (within experimental error) at the same rate as the *X* peak.

The absorption spectrum of the Adamson preparation was taken with a Cary spectrophotometer and showed maxima at 375 and 310 mμ and minima at 360 and 285 mμ. An attempt was made to recover crystalline potassium pentacyano monaquo cobaltate-III from the Adamson preparation through the addition of alcohol and strong cooling. However, the product which crystallized out was shown by ionography to contain only a small portion of the desired ionic species, along with two other species, one of which was $Co(CN)_6^{=}$.

The RÂY *et al.* synthesis[11] of tetracyano diaquo cobaltate-III was also carried out and yielded a solution containing a noncrystallizable ionic species which moved at about the same rate as the *A* peak in dissolved irradiated potassium cobalticyanide. In this connection it is interesting that an Adamson-type synthesis in which radioactive cobalt was oxidized by air in the presence of only $3CN^-/Co^{++}$ also yielded

[11] P. RÂY and N. K. DUTT *Z. anorg. Chem.* **234,** 65 (1937); P. RÂY and T. GUPTACHAUDHURI *ibid.* **220,** 154 (1934); P. RÂY and S. Ch. CHACKRABARTY *ibid.* **211,** 173 (1933); P. RÂY and S. N. MAULIK *ibid.* **199,** 353 (1931); P. RÂY *J. Ind. Chem. Soc.* **4,** 325 (1927).
[12] H. BASSETT and A. S. CORBET *J. Chem. Soc.* **125,** 1358 (1924).
[13] E. MÜLLER and H. LAUTERBACH *Z. anal. Chem.* **62,** 25 (1923); E. MÜLLER and W. SCHLUTTIG *Z. anorg. Chem.* **134,** 333 (1924).
[14] A. W. ADAMSON *J. Amer. Chem. Soc.* **78,** 4260 (1956); A. W. ADAMSON *Rec. trav. chim.* **75,** 809 (1956); A. W. ADAMSON *J. Amer. Chem. Soc.* **73,** 5710 (1951).
[15] D. N. HUME and I. M. KOLTHOFF *J. Amer. Chem. Soc.* **71,** 867 (1949).
[16] L. C. SMITH, J. KLEINBERG, and E. GRISWOLD *J. Amer. Chem. Soc.* **75,** 449 (1953).

about 10% of a species separable from the penta- and hexa-cyano ions by paper electrophoresis and moving at a velocity comparable with that of the *A* peak. Work on syntheses similar to this is continuing. We feel that at present the species $Co(CN)_4(H_2O)_2^-$ may be tentatively identified with the *A* peak.

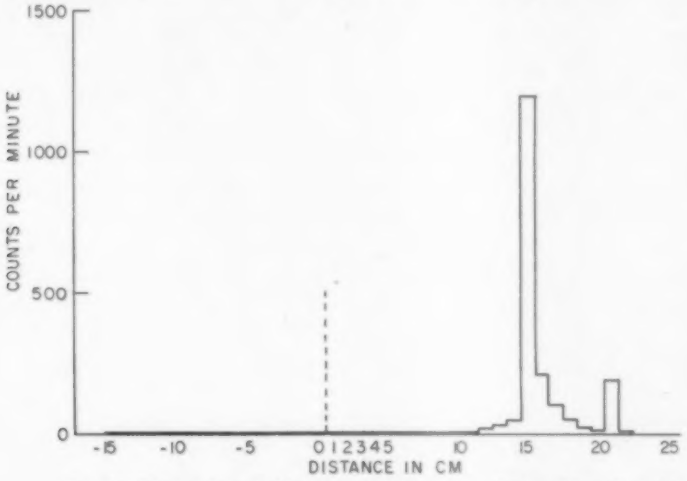

FIG. 6.—Electrophoresis histogram: Adamson-synthesis with radioactive cobaltous nitrate and cyanide, $6CN^-/Co^{++}$.

To study the effect of the pH of the solution in which the irradiated salt was dissolved, a series of runs were made in the following media: 1 F nitric acid, pH 5·4 buffer and 4×10^{-3} F sodium hydroxide. Histograms similar to Fig. 4 were obtained, but the relative activities in the different peaks were altered. In the case of the sodium

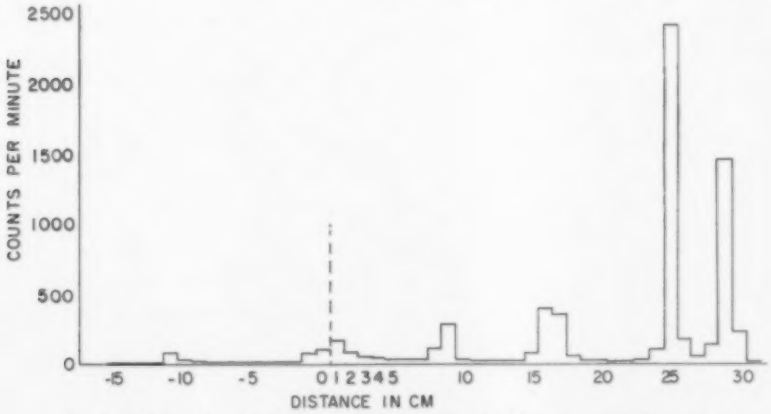

FIG. 7.—Electrophoresis histogram: crystals dissolved in concentrated ammonia.

hydroxide solutions the "cobaltous" peak of course remained at the origin owing to the neutrality of the cobalt hydroxide produced.

When the irradiated crystals were dissolved in concentrated ammonia and ionographed, on paper wet with either pH 5·4 buffer or dilute ammonia, the rather surprising distribution presented in Fig. 7 was obtained. There is very little cationic

cobalt present, and a new peak has appeared to the left of the parent, *X* and *A* peaks. It was demonstrated in separate experiments that cobalticyanide is stable in concentrated ammonia and moves in the normal way on paper wet with dilute ammonia. It was also shown that labelled cobaltous ion, when ionographed in dilute ammonia after dissolution in concentrated ammonia, moves so slowly in the cation direction that it remains essentially fixed at the origin. In such solutions a mixture of cobaltous and cobaltic aquo-pentamines and hexamines are probably present. An upper limit of about 10% can be set on the total cationic cobalt present in concentrated ammonia solutions compared with 50–55% in pH 5·4 buffer. Experiments in dilute (1·6 F) ammonia gave histograms similar to those obtained with dilute sodium hydroxide, in that the new anion peak (which we designate the *B* peak) was not observed, while the *X* peak was very large.

Finally, samples of irradiated crystals were annealed either thermally or by long standing at dry-ice or room temperature, and ionographed after dissolution in several media. As expected, the results indicated an increase in cobalticyanide and a decrease in cobaltous ion on annealing. The *X* and *A* peaks also showed changes, but relatively smaller than that of the parent ion. The results of all electrophoresis experiments are given in Tables 2, 3, and 4.

TABLE 3.—PERCENTAGE DISTRIBUTION OF IONIC SPECIES IN IRRADIATED $K_3Co(CN)_6$ AS A FUNCTION OF CONDITIONS OF DISSOLUTION: FRESHLY-BOMBARDED CRYSTALS

Conditions of dissolution	$Co(CN)_6^{---}$	$Co(CN)_5(H_2O)^{--}$	$Co(CN)_4(H_2O)_2^{-}$	$Co(CN)_4(NH_3)_2^{-}$	Co^{++}	Unaccounted for
1 F NHO_3	20	13	6	—	54	7
pH 5·4	19	16	6	—	55	4
Dilute NaOH	24	39	11		22	4
Conc. NH_4OH	27[a]	41	14	8	10	—
Conc. NH_4OH	[b]				12	

[a] When this run was made the sample had been stored for 2 months at dry-ice temperature and had annealed slightly. A run at the same time with the same sample in pH 5·4 buffer gave $Co(CN)_6^{---}$ = 26%. See Table 2.

[b] The anion peaks were not sufficiently well resolved to permit determination. The condition of anneal in this sample was comparable to that in the "dilute NaOH" sample.

TABLE 4.—PERCENTAGE DISTRIBUTION OF IONIC SPECIES IN IRRADIATED $K_3Co(CN)_6$ AS A FUNCTION OF CONDITIONS OF DISSOLUTION: ANNEALED CRYSTALS

Conditions of dissolution	$Co(CN)_6^{---}$	$Co(CN)_5H_2O^{--}$	$Co(CN)_4(H_2O)_2^{-}$	$Co(CN)_4(NH_3)_2^{-}$	Co^{++}	Unaccounted for
1 F HNO_3	42	13	5	—	38	2
0·05 F $HClO_4$	38	14	5	—	36	7
pH 5·4 buffer	44	14	3	—	38	1
	42	16	3	—	38	1
	43	11	4	—	35	7
Dilute NaOH	44	40	5	—	8	3
Dilute NH_4OH	45	40	7	—	3	5
Conc. NH_4OH	43	43	7	3	4	0
	44	36	7	6	7	0

DISCUSSION

From the electrophoresis data alone we may make the following statements toward the construction of a model for the distribution of fragments in the freshly-bombarded and annealed crystals and the reactions of such fragments in water.

(1) For a given lot of irradiated crystals in a given state of anneal, the percentage activity observed in the parent, cobalticyanide, remains constant within experimental error over a wide range of conditions of dissolution, i.e. 1 F nitric acid, pH 5·4 buffer, dilute sodium hydroxide, dilute and concentrated ammonia. This suggests that the activity found in the parent electrophoresis peak actually represents hexacyano fragments present as such in the irradiated crystal. Since HUME and KOLTHOFF[16] showed that $Co(CN)_6^{\equiv}$ is probably unstable in water with respect to $Co(CN)_5^{=}$, and since the latter is oxidized to $Co(CN)_5H_2O^{=}$, it would seem to be true that the hexacyano fragments in the crystal contain cobalt-III and not cobalt-II.

(2) When the irradiated crystals are dissolved in concentrated ammonia rather than pH 5·4 buffer, the cationic fraction drops from something over 50% to about 10%. This decrease reappears as anionic species, and if hydroxyl is assumed to be absent from the sixfold co-ordination sphere* then the species produced (*X*, *A*, and *B*) must have four or five cyanides per cobalt.

The simplest interpretation is that the fragments present in the crystal have the same number of cyanides per cobalt as the ions observed in solution. This assumption cannot be proved by the data obtained here, however, there is evidently insufficient free cyanide in the solution of the irradiated salt to react with the minute amount of cobaltous ion formed, and we thereby infer that the free cyanide is also too small to cause reactions of the type

$$Co(CN)_5^{=} + CN^- \longrightarrow Co(CN)_6^{\equiv}$$

in solution. Also, the proportion of $Co(CN)_6^{\equiv}$ to $Co(CN)_5H_2O^{=}$ in solution is very little changed in going from pH 5·4 to 1 F acid, even though the concentration of free cyanide ion is reduced by about 10^5.

The total probability that cobalt recoil leads to fragments having four, five, or six cyanides is seen to be about 90%. Since only about 40% of the activity appears in acid solutions as tetra-, penta-, and hexacyano complex ions, it is evident that the penta- and/or tetracyano fragments in the crystal can react with water to produce cobaltous ion by alternative reaction paths. Since the proportion of pentacyano monaquo cobaltate-III observed depends on the pH of dissolution, it is evident that at least one of the competing reactions (hydration or reduction) is pH-dependent in this case.

The explanation involving competing hydration and reduction reactions is formally similar to that invoked by LIBBY[17] in the interpretation of manganese hot-atom recoils in irradiated potassium permanganate.

(3) The species responsible for the *B* peak almost certainly contains NH_3 in its

* Anions containing a cobalt-III nucleus with hydroxyl in the co-ordination sphere are known to form by reactions such as $Co(NH_3)_5H_2O^{+++} + OH^- \rightarrow Co(NH_3)_5OH^{++} + H_2O$ (N. V. SIDGWICK *Inorganic Chemistry* Vol. II, p. 1402). Oxford (1950). However, we have not considered species such as $Co(CN)_5OH^{\equiv}$ as candidates for the *X* or *A* peaks for two reasons: (1) The rate of reactions such as the one written falls off sharply as one goes to lower positive charges in the complex ion, and (2) both *X* and *A* continue to appear as stable entities even in 1 F acid solutions.

[17] W. F. LIBBY *J. Amer. Chem. Soc.* **62**, 1930 (1940).

co-ordination sphere, as it is formed only in concentrated ammonia solutions but not in sodium hydroxide solutions of the same pH. Since it is an anion, it must also contain four or five cyanides; i.e. it must be $Co(CN)_5(NH_3)^{=}$, $Co(CN)_4(NH_3)_2^{-}$, or $Co(CN)_4(NH_3)(H_2O)^{-}$. The *B* peak was not produced by an experimental air-oxidation of $Co(CN)_5^{=}$ in concentrated ammonia solution, whereas oxidation of this species by Br_2 or I_2 produces $Co(CN)_5Br^{=}$ and the corresponding iodide.[14] This is of course not conclusive evidence against $Co(CN)_5NH_3^{=}$. We will assume, however, that the *B*-peak species is a tetracyano diamino cobaltate-III, since this assignment is consistent with the observed distribution of fragments (Table 7).

(4) The annealing process can be described by two equations:

$$Co(CN)_4^{-} + CN^{-} \longrightarrow Co(CN)_5^{=} \quad (4)$$

$$Co(CN)_5^{=} + CN^{-} \longrightarrow Co(CN)_6^{=} \quad (5)$$

The electrophoresis data on annealed crystals show that the increase in $Co(CN)_6^{=}$ on annealing is not accompanied by an equivalent decrease in $Co(CN)_5^{=}$, and hence if equation (5) is operative during the annealing process, equation (4) must be also. Alternatively, $Co(CN)_6^{=}$ may be formed during annealing by a process different from equation (5). The data are not sufficiently accurate or detailed to permit the calculation of activation energies for reactions (4) and (5), however; the shapes of the annealing curves (Figs. 1, 2, and 3) are such that they cannot be fitted by any single exponential expression. The annealing curves are unfortunately of little use in understanding the mechanism of annealing, since, as has been pointed out, the cobalt α-nitroso β-naphthol method determines a "retention" which is the sum of the $Co(CN)_6^{=}$ and $Co(CN)_5(H_2O)^{=}$, while the latter is generated by a pH-dependent reaction.

It has been possible to set up hypothetical distributions of fragments in the freshly-bombarded and annealed crystals which will produce the observed distributions of hexacyano, pentacyano monaquo, tetracyano diaquo, tetracyano amine, and cobaltous ions in solution, including the requirement that both $Co(CN)_5^{=}$ and $Co(CN)_4^{-}$ in the crystal are subject to pH-dependent competing hydration and reduction reactions. The hypothesized reactions in water are given in Table 6.

The numbers given as the fraction of fragments reacting by a given path are of necessity approximate figures; the data do not permit a very precise calculation of these numbers. They were chosen to fit the data and imply the following chemical properties for the partially-stripped cyano-fragments: $Co(CN)_4^{-}$ is more easily reduced than $Co(CN)_5^{=}$ at a given pH, and each fragment is more easily reduced, the more acid the solution. Hydration of $Co(CN)_5^{=}$ to $Co(CN)_5(H_2O)^{=}$ is complete in alkaline solutions.

The distributions given in Table 5 may be assumed for freshly-bombarded (dry-ice), partially annealed (2 months at −78°C), and annealed (1 hour at 100°C or 3 months at room temperature) crystals. Such distributions reacting in water according to the reaction paths given in Table 6 give, within the rather large experimental error, the observed distributions of ionic species in the aqueous solutions. It should be emphasized that the distributions and reaction path fractions are not completely unique; small changes in both can be accommodated within the experimental errors. Also, the distributions add up to only 95%, as roughly 5% of the activity was usually not assignable to any peak in the electrophoresis pattern.

TABLE 5.—INFERRED PERCENTAGE DISTRIBUTION OF FRAGMENTS IN IRRADIATED $K_3Co(CN)_6$ CRYSTALS

	$Co(CN)_6^{---}$	$Co(CN)_5^{--}$	$Co(CN)_4^{-}$	Co^{++}, lower cyanides
Freshly-bombarded	19	43	28	5
Partially annealed	26	41	24	4
Annealed	44	35	14	2

TABLE 6.—INFERRED REACTIONS OF FRAGMENTS IN IRRADIATED $K_3Co(CN)_6$ DURING AQUEOUS DISSOLUTION

Conditions of dissolution	Fragments in crystal	Fraction reacting by indicated path	Species in water[a]
All	$Co(CN)_6^{---}$	1· →	$Co(CN)_6^{---}$
pH = 5·4	$Co(CN)_5^{--}$	·37 →	$Co(CN)_5H_2O^{--}$
		·63 →	Co^{++}
Alkaline and conc. ammonia	$Co(CN)_5^{--}$	1· →	$Co(CN)_5H_2O^{--}$
pH = 5·4	$Co(CN)_4^{-}$	·21 →	$Co(CN)_4(H_2O)_2^{-}$
		·79 →	Co^{++}
Alkaline	$Co(CN)_4^{-}$	0·5 →	$Co(CN)_4(H_2O)_2^{-}$
		·5 →	Co^{++}
Conc. ammonia	$Co(CN)_4^{-}$	0·5 →	$Co(CN)_4(H_2O)_2^{-}$
		·25 →	Co^{++}
		·25 →	$Co(CN)_4(NH_3)_2^{-}$
All	Co^{++}, Co^{+++}, Co, and lower cyanides	1· →	Co^{++}

[a] Cobaltous ion is observed in the electrophoresis experiments. If cobaltic ion $Co(H_2O)_6^{+++}$ were formed by loss of cyanide from the tetra- and pentacyano fragments, it would very likely be reduced to cobaltous on the paper. We cannot distinguish between this process and the direct reduction of cobaltic fragments to cobaltous in solution.

TABLE 7. COMPARISON OF CALCULATED AND OBSERVED DISTRIBUTION OF IONIC SPECIES FROM IRRADIATED $K_3Co(CN)_6$ DISSOLVED IN AQUEOUS SOLUTIONS

State of anneal	Conditions of dissolution		$Co(CN)_6^{---}$	$Co(CN)_5H_2O^{--}$	$Co(CN)_4(H_2O)_2^{-}$	$Co(CN)_4(NH_3)_2^{-}$	Co^{++}
Freshly bombarded	pH 5·4	calc.	19	16	6	—	54
		obs.	19	16	6	—	55
	dil. NaOH	calc.	19	43	14	—	19
		obs.	24	39	11	—	22
Partially annealed (2 months at −78°C)	pH 5·4	calc.	26	15	5	—	49
		obs.	26	16	3	—	52
	conc. NH_4OH	calc.	26	41	12	6	16
		obs.	27	41	14	8	10, 12
Annealed to plateau (stored at room temperature for 3 months or heated for 1 hour at 100°C)	pH 5·4	calc.	44	13	3	—	35
		obs.	44, 42, 43, 42[a]	14, 16, 11, 13	3, 3, 4, 3	—	38, 38, 35, 38
	dil. OH^-	calc.	44	35	7	—	9
		obs.	44, 45[b]	40, 40	5, 7	—	8, 3
	conc. NH_4OH	calc.	44	35	7	4	5
		obs.	43, 44	43, 36	7, 7	3, 6	4, 7

[a] First three numbers in each column refer to samples stored at room temperature. Fourth number refers to a sample heated at 100°C.
[b] First number in each column refers to dilute NaOH; second number refers to dilute NH_4OH.

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To recapitulate, the model here suggested assumes a certain primary distribution of radioactive cobalt among the several species: (1) $Co(CN)_6^{=}$, (2) $Co(CN)_5^{=}$, (3) $Co(CN)_4^{-}$, and (4) lower complexes and uncomplexed cobalt. Because of the known stability of $Co(CN)_6^{=}$ it may be assumed *a priori* that the amount of this species is not altered by dissolution in water; the data support this view. It is also assumed that the species listed under (4) all produce cobaltous ion on dissolution. In order to specify the fate of the $Co(CN)_5^{=}$ and $Co(CN)_4^{-}$ entities in the crystal, it is necessary to introduce parameters whose values depend on the conditions of dissolution; these parameters describe the relative probabilities of hydration, ammination (in the case of $Co(CN)_4^{-}$), and reduction. The number of adjustable parameters so employed is three. A comparison of the calculated and observed distributions is given in Table 7, and it is seen that there is good agreement.

It is fundamental to this model for the annealing process that a cyanide recombines with a cyanocobalt fragment. We discount processes such as

$$Co(CN)_4^{-} + Co(CN)_6^{=} \longrightarrow 2Co(CN)_5^{=} \qquad (6)$$

which would seem to require large activation energies due to the necessity of breaking Co-CN bonds.

It is interesting that the annealing process does not appear to go to completion; even in crystals which have been annealed to the plateau values $Co(CN)_5^{=}$ and $Co(CN)_4^{-}$ fragments are still present. However, there seems to be no *a priori* reason to expect that all cobalt recoils are inherently annealable. In some of the regions of local damage around radioactive atoms, two cyano groups may have combined to give cyanogen, thus restricting the annealing process. We have assumed (equations 4 and 5) that cyanide ions, rather than free radicals, are responsible for the observed reformation of hexacyanide ion during the annealing process. It is of course possible to write equations similar to (4) and (5) with free radical CN successively oxidizing the tetra- and pentacyano cobaltates from the uni- to the trivalent state. Information concerning the reaction of $Co(CN)_5^{=}$ with, for example, air in slightly acidic solutions might help to resolve the question, for if $Co(CN)_5^{=}$ can be shown to produce Co^{++} as well as $Co(CN)_5(H_2O)^{=}$ at pH 5, then a good case can be made that the pentacyano fragments in the crystal contain cobalt-II, and these are oxidized during annealing by cyanide free radical. However, in one experiment in which the irradiated salt was dissolved in a solution containing an oxidizing agent, ferricyanide, no change was observed in the distribution of ionic species formed.

We have not attempted to give any sort of mechanical model of the actual recoil process leading to the distribution of cyanocobalt fragments in the crystal. In the first place, roughly one-third of the neutron-capture events in cobalt-59 lead to the 11-min isomeric state in cobalt-60, in whose decay internal conversion predominates.[18] Also, the spectrum of capture gamma rays is not fully established so that one cannot calculate a distribution of cobalt-60 recoil energies.

The results of our experiments with potassium cobalticyanide find a close parallel in those of ZUBER[1] with cobaltic trisethylenediamine salts. He also observed that, besides cobaltous ion and the parent, additional cobalt-containing complex species appeared to be present in the bombarded crystal and, like our pentacyano fragments, their percentage remained roughly constant on annealing. Such a close similarity

[18] M. GOLDHABER and A. W. SUNYAR *Phys. Rev.* **83**, 906 (1951).

can hardly be fortuitous and may be taken to indicate that in this positive co-ordination complex of cobalt, metastable, partially-stripped fragments are also important recoil products.

THE USE OF POTASSIUM COBALTICYANIDE IN THE PREPARATION OF ^{60}Co OF HIGH SPECIFIC ACTIVITY

The availability of high-flux reactors makes the point somewhat academic, but the Szilard-Chalmers process in potassium cobalticyanide affords a means for the preparation of enriched cobalt-60. Samples of irradiated salt were dissolved in ammonium thiocyanate solutions, which were then extracted with amyl acetate. Two samples of pile-bombarded crystals (of the order of a gram each) yielded enriched cobalt-60 as follows:

(1) A 5-day bombardment near the centre of the pile (Cd ratio 2, flux $3{\cdot}6 \times 10^{12}$ n/cm^2 sec) gave 1·42 millicuries at a specific activity of 1·9 mc/mg.

(2) A 5-day bombardment away from the central loading, but in the graphite (Cd ratio 25, flux 1×10^{12}) gave 1·56 mc, at 5·8 mc/mg specific activity.

Since pure cobalt-60 is about 310 mc/mg, the richer of these two preparations contains about one atom of cobalt-60 to fifty-four atoms of inert cobalt, which indicates a remarkable stability of potassium cobalticyanide to radiation decomposition. Presumably even higher specific activities could be attained through bombardment at dry-ice temperature.

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INFRA-RED SPECTRA OF QUINOL CLATHRATE COMPOUNDS*

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Abstract—The ease of synthesis of "inclusion compounds" of hydroquinone with small molecules, such as HCl, H_2S, SO_2, and CO_2, affords a unique opportunity to study restricted rotational and translational motion of such molecules, as well as to elucidate the nature of the binding of the lattices of such compounds. Spectra, both absorption and differential, of such compounds, when suspended in KBr pellets, covering the range 1·1–15 μ, are reported, which are in agreement with the difference in crystal structure between α-hydroquinone and its β allomorph originally proposed by PALIN and POWELL. In addition, some results are presented which indicate the extent of freedom of rotational motion of the small molecules included in the clathrate, and the extent of the binding of the small molecules to the clathrate lattice.

THE history, nature, and general principles of preparation of "inclusion compounds" of hydroquinone with various small molecules, such as HCl, H_2S, SO_2, and CO_2, have received excellent discussion and elucidation in the recent researches of H. M. POWELL and co-workers.[1] The entire subject has been recently reviewed by CRAMER.[2]

The existence of such compounds affords a unique opportunity for the study of restricted rotational and translational motion of the small molecules—those which are included in the hydroquinone clathrate—without resorting to low temperatures. In addition, unlike the situation in the usual condensed state, the small molecule is still rather isolated—at least from others of its own kind.

Although POWELL's investigations have both wide in scope and thorough, there exists little information on the degree of freedom of the captured molecules. The fact that in the SO_2-clathrate this normally asymmetric molecule (symmetry group C_{2v}) was found to occupy a site of symmetry C_i‡ suggested to POWELL that in the clathrate, the SO_2 molecule was freely spinning about an axis perpendicular to its twofold axis, but lying in the plane of the molecule. If this were indeed true, appropriate spectroscopic investigation of the clathrate should demonstrate the feature commonly associated with the existence of such motion—a rotational fine structure in the spectrum. To be more specific, by appropriately choosing the small molecule, namely by choosing those which have the least and smallest moments of inertia and whose fundamental vibration frequencies do not coincide with those of hydroquinone, it

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‡ See reference 1(a), p. 209.

[1] (a) D. E. PALIN and H. M. POWELL *J. Chem. Soc.* 208–21 (1947).
(b) H. M. POWELL *Proc. Intern. Cong. of Pure and Applied Chem.* **XI**, No. 1, 585, (1947).
(c) H. M. POWELL, *J. Chem. Soc.* 61 (1948).
(d) D. E. PALIN and H. M. POWELL *J. Chem. Soc.* 571 (1948).
(e) D. E. PALIN and H. M. POWELL *J. Chem. Soc.* 815 (1948).
(f) H. M. POWELL and M. GUTER *Nature* **164**, 240 (1949).
(g) H. M. POWELL *J. Chem. Soc.* 298 (1950).
(h) H. M. POWELL *J. Chem. Soc.* 468 (1950).
[2] F. D. CRAMER *Rev. of Pure and Applied Chem.* **5**, 143 (1955).

would be possible, assuming some freedom of rotation, to observe a rotation-vibration spectrum, much like that of the gas of the small molecules itself.

If, on the other hand, no fine structure is observed, but only the characteristic vibrational spectrum of a molecule in a condensed state, it may be concluded that the rotational and translational motion of the molecule as a whole is hindered. The extent of such hindering may even be estimated, should the fine structure be absent, from the breadth of the vibration band, using the model of collisional perturbation as the cause of band breadth[3] calculating the effective collision diameter and comparing it to that determined by X-ray diffraction techniques.*

Finally, if the binding is less physical (restriction of motion) and more chemical, this too would be recognizable spectroscopically, as "characteristic frequencies" of functional groups created in the formation of the clathrate would develop spectroscopic activity in their usual manner.

EXPERIMENTAL

The clathrates used in this study were the β-hydroquinone clathrates with HCl, H_2S, CO_2, and SO_2 as the included molecules. The methods of preparation were similar to those described by PALIN and POWELL.[1e]

Spectra were obtained by suspending the samples in so-called "KBr-pellets", according to the technique devised by SCHIEDT[4a] and STIMSON and O'DONNELL.[4b] Unless the sample was extremely well pulverized, there was much difficulty encountered in obtaining "scatter-free" spectra, due to the action of an extreme example of the Christiansen effect first noted in the infra-red by PRICE and TETLOW.[5] Even then, there is much loss of energy due to scattering in the 1–2-micron region.

The instrument used for the major portion of this work was a Perkin-Elmer Model 21 spectrophotometer equipped with NaCl optics. The 1–2-μ region was investigated with a Beckman D. K. spectrophotometer, equipped with a quartz prism, while the high-resolution spectra in the 2300–2350-cm^{-1} region were obtained using a Perkin-Elmer Model 13 spectrophotometer, equipped with KBr optics, whose Littrow mirror was replaced with a "Merton-N.P.L." 7500-l.p.i. grating, obtained through the courtesy of the Light Division, National Physical Laboratories, Teddington, England.

RESULTS AND DISCUSSION

Spectra of HCl and H_2S clathrates are shown in Fig. 1, while those of the HCl clathrate and α-hydroquinone are compared in Fig. 2. Inspection of these two figures leads to the conclusion that either the guest molecules have been chemically changed, i.e. chemically bound to the clathrate lattice, so that they have lost their former identities,* or that they are present in insufficiently small quantities for detection. If the former explanation is correct, the spectra could show evidences of the new functional groups formed in the reaction. However, what is observed is not new bands, but that absorption maxima at 1260, 811, and 703 cm^{-1} in the α-quinol spectrum are *missing* in the spectrum of both clathrates. On the other hand, the amounts of guest molecules present correspond, in each case, to less than 5% of the usual amounts necessary to obtain decent spectra of gaseous HCl and H_2S, respectively, so that the second explanation is favoured.†

* Reference 1(a), p. 221.

† It is to be noted that HCl and H_2S are (a) weak absorbers in the infra-red and (b) most of their fundamentals are badly overlapped by the strong bands of hydroquinone.

[3] (a) D. A. RAMSAY *J. Amer. Chem. Soc.* **74**, 72 (1952).
(b) T. L. BROWN *J. Chem. Phys.* **24**, 1281 (1956).
[4] (a) U. SCHIEDT *Z. Naturforsch.* **76**, 220 (1952); **86**, 66 (1953).
(b) M. M. STIMSON and M. J. O'DONNELL *J. Amer. Chem. Soc.* **74**, 1805 (1952).
[5] W. C. PRICE and K. S. TETLOW *J. Chem. Phys.* **16**, 1157 (1948).

Nevertheless, it is quite clear, from Figs. 1 and 2, that in accepting the guest molecules (HCl and H_2S), the quinol *crystal structure* is profoundly changed, for the spectrum of the clathrate is poorer in bands than that of the pure hydroquinone. In fact, this *direction* of change is completely consistent with POWELL's findings,[1a,b] as it corresponds to an *increase* in symmetry for the environment of a quinol molecule

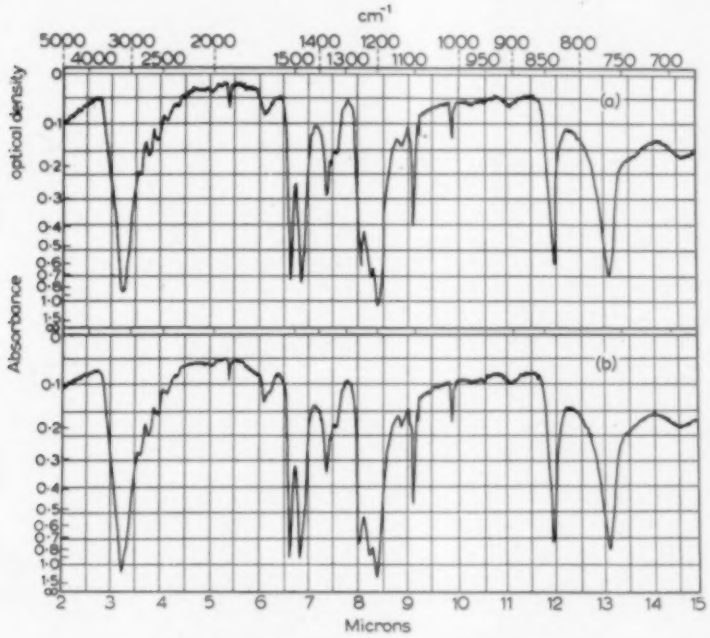

FIG. 1.—(a) Sample: hydroquinone–H_2S clathrate.
Phase: Solid (KBr pellet).
(b) Sample: hydroquinone–HCl clathrate.
Phase: Solid (KBr pellet).

as it goes to the clathrate structure. α-Quinol crystallizes in space group $R3 = C_{3i}^1$, while the characteristic clathrate space group is $R\bar{3} = C_{3i}^2$, which differs from the former in having a centre of symmetry. Furthermore, inspection of Fig. 1 demonstrates that this change is independent of the specific guest molecule, as the spectra of the HCl clathrate and of the H_2S clathrate are virtually identical, while quite different from that of α-hydroquinone.

While the actual amounts of HCl and H_2S present in the samples were small, it would in fact be difficult to observe significant "rotation-vibration" spectra, as most of their fundamentals overlap badly with strong bands of hydroquinone. Recourse was therefore along the following directions: (1) increase in concentration of clathrate in the KBr pellet; (2) investigation of the near infra-red region, where hydroquinone absorbs little; (3) investigation, still in the infra-red, of stronger absorbers than HCl and H_2S, and/or those whose fundamentals lie in the more or less transparent regions of hydroquinone spectrum, such as SO_2 and CO_2.

The first procedure is difficult, as it adds to those already discussed in connection with the encounters with the Christiansen effect. To be specific, with more than 7 mg

of clathrate/KBr pellet, no amount of grinding of sample could eliminate the large scattering losses. The spectra illustrated are of samples containing ~2·5 mg of clathrate/KBr pellet. Another method would be to increase the stoichiometric concentration of gas molecules in the clathrate. The present model [2] of these compounds would exclude this possibility: the upper limit in this concentration is best represented

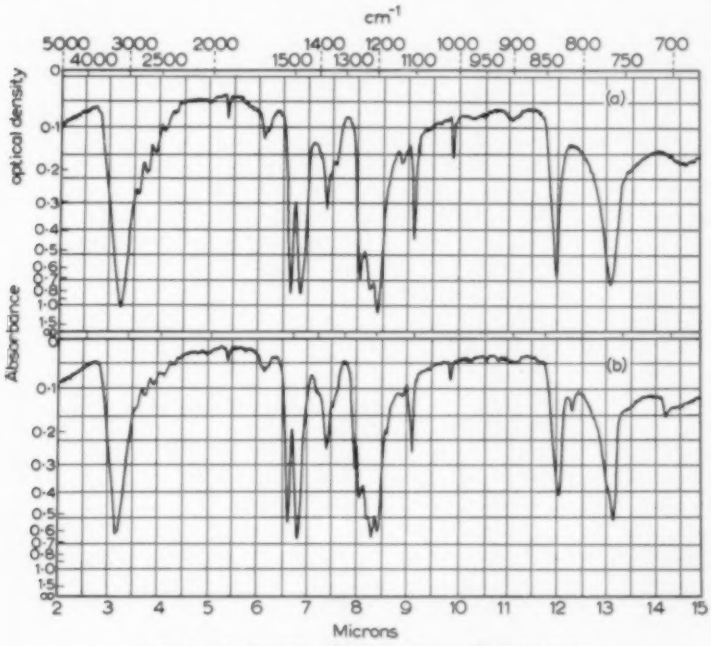

FIG. 2.—(a) Sample: β-hydroquinone–HCl clathrate.
Phase: Solid (KBr pellet).
(b) Sample: α-hydroquinone.
Phase: Solid (KBr pellet).

by the formula $3C_6H_4(OH)_2 \cdot M_x$, where M represents the included molecule and $0 \leq x \leq 1$; our analyses indicated that in our preparation, $x \cong 1$.

The second procedure was fruitful, but is somewhat questionable. Spectra in the 1·1–2·0-μ region are shown in Fig. 3 and Fig. 4. The spectra of both clathrates and of α-quinol by themselves (Fig. 3) show little but the scattering loss mentioned previously. However, "differential spectra," of the HCl clathrate vs. α-hydroquinone *or* of the HCl clathrate vs. that of the H_2S clathrate as references, each demonstrate complex patterns in the recorded quantity of (energy transmitted by HCl-clathrate)/(energy transmitted by the reference) in the vicinity of 5340 and 7240 cm^{-1}. These were completely reproducible, using other pellets and clathrate preparations, while no similar patterns were observed using the H_2S clathrate vs. α-hydroquinone or different α-hydroquinone pellets vs. one another. The first and second overtones of gaseous HCl fall at 5668 and 8347 cm^{-1} respectively.[6] It is possible to interpret these patterns as these overtones, shifted to lower frequencies by the "semi-binding" of HCl molecule, although it should be pointed out that his procedure amounts to little more

[6] G. HERZBERG *Spectra of Diatomic Molecules* p. 55. D. Van Nostrand, New York (1950).

than recording the spectrum at a high gain, and therefore the recorded "patterns," although reproducible, are still somewhat questionable. Why they are not observed in the H_2S spectra, such as in that of the H_2S clathrate vs. α-hydroquinone, is not clear; this may be because of the exceedingly weak characteristic absorption of this gas in the near infra-red.[7]

The third procedure was indeed the most valuable. The spectrum of the SO_2 clathrate is shown in Fig. 5. Examination of the 1200, 800, and 700-cm^{-1} regions demonstrate that the crystal structure of this clathrate is indeed that of β-hydroquinone, again confirming POWELL's work.[1a,b] In addition, a strong new band appears at 2915 cm^{-1}. A more concentrated pellet (spectrum shown by broken line in Fig. 5) demonstrates another new band, hinted at in the spectrum of the more dilute sample, at 1344 cm^{-1}. The fundamentals of SO_2 are at 519, 1151, and 1361 cm^{-1}*. Overtones

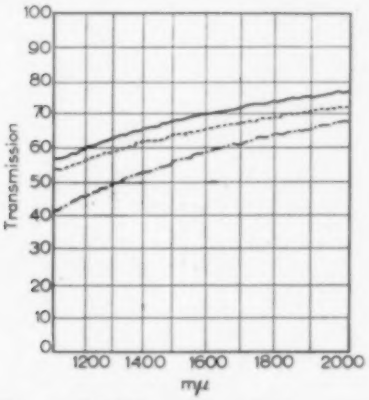

FIG. 3.—Solid Phase (KBr pellets).
Sample: ——— α-hydroquinone
- - - - - - β-hydroquinone–HCl clathrate
- — - β-hydroquinone–H_2S clathrate.

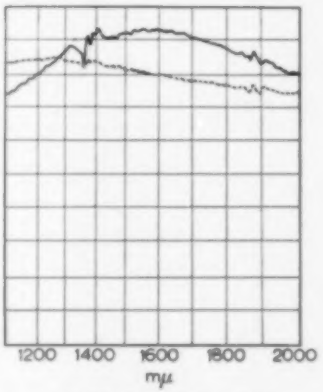

FIG. 4.—Solid phase (KBr pellets).
Sample: ——— β-hydroquinone–HCl clathrate with α-hydroquinone in reference beam
- - - - - β-hydroquinone–HCl clathrate with β-hydroquinone–H_2S in the reference beam.

and combinations have been observed at 1871, 2305, and 2499 cm^{-1}*. There is thus a near coincidence with one fundamental, while the others lie either in unexamined regions or in regions obscured by absorption by hydroquinone. The very strong band at 2915 does not agree with any of the definitely assigned overtones or combinations, but it is possible to assign it as the ternary combination of the three fundamentals. Bands in this region for gaseous SO_2 were reported by COBLENTZ[8] but could not be reproduced by BAILEY *et al.*[9] although they recognized the possibility of assigning the Coblentz-observed bands in this manner.

What are thought to be the most significant results of this study were obtained with the CO_2 clathrate. The low-dispersion spectrum of this clathrate is shown in Fig. 6, along with those of the HCl clathrate and of α-hydroquinone. There is a definite

* Reference 7, p. 285.

[7] G. HERZBERG *Infrared and Raman Spectra of Polyatomic Molecules* p. 283. D. Van Nostrand, New York (1945).

[8] W. W. COBLENTZ *Investigations of Infra-red Spectra, Part I* pp. 52 and 177. Carnegie Institution of Washington Publication, 35 (1905).

[9] C. R. BAILEY, A. B. C. CASSIE, and W. R. ANGUS *Proc. Roy. Soc.* **A130**, 142 (1930).

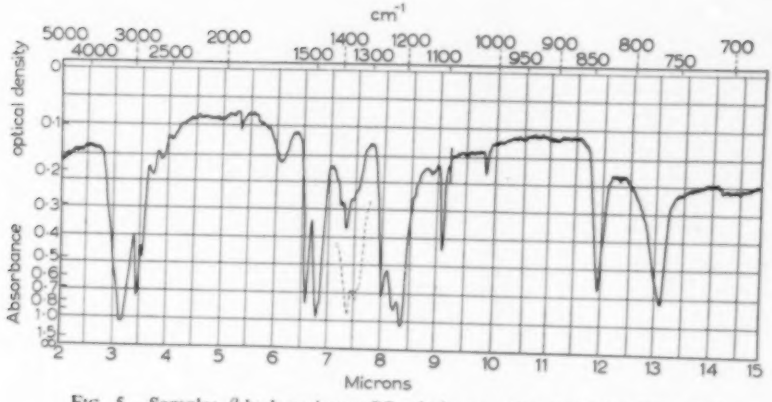

FIG. 5.—Sample: β-hydroquinone–SO_2 clathrate. Phase: Solid (KBr pellet).

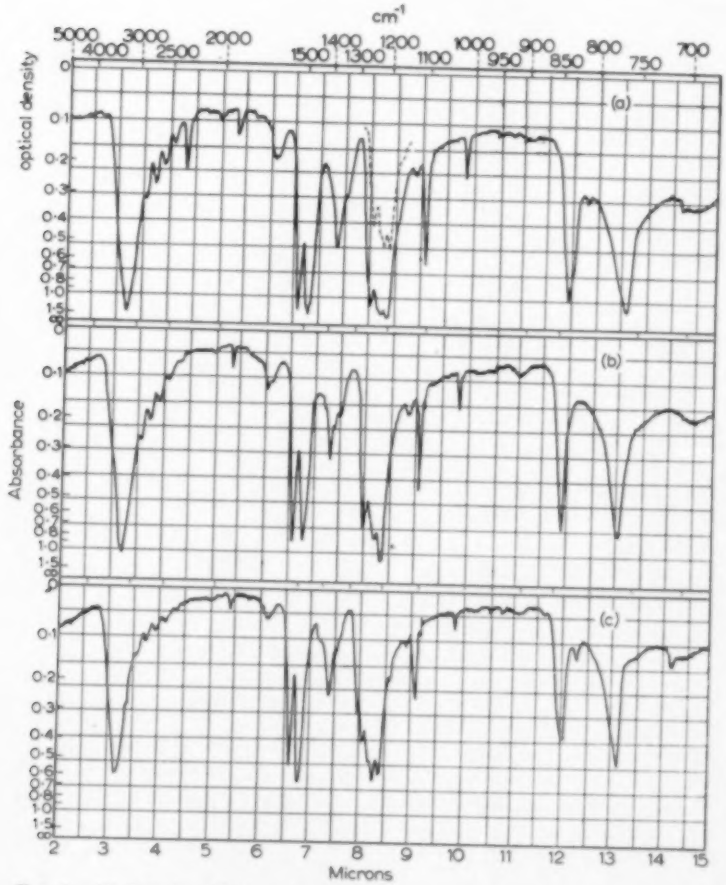

FIG. 6.—(a) Sample: β-hydroquinone–CO_2 clathrate Phase: Solid (KBr pellet).
(b) Sample: β-hydroquinone–HCl clathrate. Phase: Solid (KBr pellet).
(c) Sample: α-hydroquinone. Phase: Solid (KBr pellet).

indication of captured CO_2 gas; the 2350-cm^{-1} parallel band of CO_2 is a prominent feature of the spectrum. The spectrum in the 600–700-cm^{-1} region (not shown) also demonstrates the strong perpendicular band of CO_2. Nevertheless, the structure of the 1200-cm^{-1} region, particularly that of a diluted sample (shown as a broken line), together with the slight absorptions in the 800- and 700-cm^{-1} regions, indicates that either this clathrate has the crystal structure of α-hydroquinone, or perhaps a crystal structure "intermediate" between that of the α and β forms, or that there is some α-hydroquinone present, as another phase. Since the two forms have a different morphology[10] (the β form is rhombohedral, while the α form is hexagonal), a microscopic examination of the CO_2-clathrate preparation was undertaken in order to separate the two phases, if such were present: it was observed that there were both needle-like and more or less rhombohedral crystals present. Spectra of the thus separated rhombohedra, suspended in KBr pellets, which should have been free of contamination by α-hydroquinone, were identical to that shown in Fig. 6.

The remaining possibility is that the CO_2 clathrate has either the α-structure, or something similar to it. The CO_2 molecule is of sufficient length (5·23 Å "long")

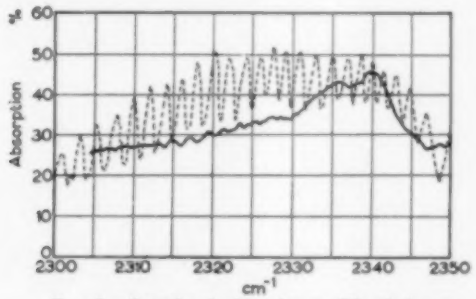

FIG. 7.—Sample: hydroquinone–CO_2 clathrate.
Phase: Solid pellet fused with KBr.
Broken line background: atmospheric CO_2 (P-branch).

that to fit the 4-Å "hole" it would have to be distorted,[1] or distort the shape of its "hole," and therefore the crystal structure. This would then account for the observed spectrum. The same distortion would be true of the SO_2 clathrate, and further inspection of Fig. 5 is consistent with this idea.

The moments of inertia of the SO_2 molecule are too great for the observation of rotation-vibration fine structure with the instruments used in this research; however, in the case of CO_2, this observation is still possible. Fig. 7 is an illustration of the grating-spectrum of the CO_2 clathrate in the vicinity of the 2350-cm^{-1} parallel band of gaseous CO^2. Atmospheric CO_2 was completely removed by flushing all housings of the spectrometer and all sample spaces with Seaford-grade nitrogen at an exceedingly rapid rate of flow. The quantitative demonstration of the success of this technique, in obtaining a "ratio" spectrum, has been indicated elsewhere.[11]

This spectrum has the form of a broad band with at least two maxima, each of which has an apparent half-width of approximately 5 cm^{-1}. The band "head" lies at 2340 cm^{-1}, about 10 cm^{-1} below the zero gap of the parallel band of the gaseous

[10] W. A. CASPARI *J. Chem. Soc.* (1926) 2944. See also ref. 1d.
[11] R. M. HEXTER *Spectrochimica Acta* (in print).

molecule. In the gas spectrum, at room temperature, the *P-R* maxima separation is about 25 cm^{-1}, so that the band at 2340 cm^{-1} in the clathrate is not assigned as the *P* branch, with the *Q* branch still forbidden. Instead, the observed band is assigned as the *Q* branch, which will be allowed for a restricted rotator,[12] while the lack of *P* and *R* branches is understandable also for the parallel band of a restricted rotator.[12]

Assuming that each of the maxima observed in this band correspond to "rotational" lines broadened by collision with the walls of the molecules' "cage," kinetic theory may be used to calculate the half-width $\Delta\tilde{\nu}_{1/2}$, from the known size of the cage. The appropriate relationship can be shown to be:[4a]

$$\Delta\tilde{\nu}_{1/2} = \frac{3}{\pi^{3/2}} \frac{(2kT)^{1/2}}{m^{1/2}ca} \tag{1}$$

where a is the diameter of the cage (4 Å), m is the particle's mass, and the other quantities have their usual significance. For $T = 300°K$, (1) gives $\Delta\tilde{\nu}_{(1/2)} = 14{\cdot}9\ cm^{-1}$. The order of magnitude of the result is therefore consistent with the interpretation of the maxima in Fig. 7 as being wall-collision-broadened rotational lines of the *Q* branch of the parallel band of the captured CO_2 molecule. In view of the shift of this branch by 10 cm^{-1} to the red, and in view of the missing *P* and *R* branches, we conclude that rotation of the CO_2 molecule in its hydroquinone clathrate is not free; there is no evidence of any greater binding.

Spectra of the CO_2 clathrate in the 600–700-cm^{-1} region (not shown) are consistent with the conclusion stated above; the perpendicular band is broadened, and its apparent centre is shifted to the red by 15 cm^{-1}. No fine structure was resolved, however, because of experimental limitations.

[12] H. H. NIELSEN *J. Chem. Phys.* **3**, 189 (1935).

J. Inorg. Nucl. Chem., 1957, Vol. 4, pp. 179 to 184. Pergamon Press Ltd., London

ÜBER METALLCARBONYLE—LXXVI[1]
ZUR KENNTNIS DES RUTHENIUMCARBONYLJODIDS

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Abstract—Under certain conditions the polymeric, diamagnetic ruthenium carbonyl iodide $Ru(CO)_2J_2$ will react with complex-forming ligands (X) having a free electron pair. In this way, with *N*-bases such as pyridine, *o*-phenanthroline and also with triphenylphosphine, -arsine, -stibine, and tri-*cyclo*hexyl-phosphine, compounds of the $RuX_2(CO)_2J_2$ type are formed which are non-electrolytes. With potassium cyanide $K_2[Ru(CO)_2(CN)_2J_2]$ a complex compound showing ionic structure is obtained. On the other hand, aromatic *iso*nitriles form tetra*iso*nitrile compounds, e.g. $Ru(p\text{-}CN\text{-}C_6H_4\text{-}OCH_3)_4J_2$, by total substitution of carbon monoxide. It is characteristic that stable complex ruthenium carbonyl iodides can only be obtained by using ligands that are bound to the metal by a mesomeric double bond.

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VOR kurzem erschien eine Abhandlung von R. J. IRVING[2] "Some Carbonyl Compounds of Ruthenium." Nachdem wir uns schon vor längerer Zeit im Anschluß an die früheren Arbeiten unseres Instituts, die erstmals dieses Gebiet behandeln,[3] mit Untersuchungen über Dicarbonylruthenium(II)-jodid befaßten, sehen wir uns veranlaßt, die Ergebnisse hierüber zu berichten. Dies erscheint umso mehr gerechtfertigt, als sich die von uns aufgefundenen Verbindungstypen in mancher Hinsicht von denen des genannten Autors unterscheiden.

Im System der Carbonylhalogenide nimmt das Ruthenium gegenüber seinen Homologen Eisen und Osmium eine Sonderstellung ein. Es bildet im allgemeinen nur Carbonylhalogenide vom Typ $Ru(CO)_2X_2$,[3] während vom Eisen[4] und Osmium[5] eine Vielfalt wohldefinierter CO-haltiger Dihalogenide existiert. So kennt man vom Eisen(II) die lückenlose Reihe der Halogenide mit 1–5 Mol CO pro Atom Eisen und vom Osmium(II) die Verbindungen mit 2–4 Mol CO pro Atom Osmium.* Ganz allgemein sind die Carbonylverbindungen der 3*d*- und 5*d*-Metalle mannigfaltiger als die der 4*d*-Metalle.

$Ru(CO)_2J_2$ ist ebenso wie $Os(CO)_2J_2$ eine chemisch sehr stabile Verbindung und unterscheidet sich darin wesentlich von dem labilen $Fe(CO)_2J_2$. Der Grund ist wohl darin zu suchen, dass erstere im Gegensatz zu $Fe(CO)_2J_2$ polymer gebaut sind,† eine Annahme, die durch eigene magnetische Messungen gestützt wird, welche ergaben,

* Von allen drei Metallen werden ausserdem Carbonylmonohalogenide beschrieben, *loc. cit.*, die jedoch gegenüber den Dihalogeniden stark in den Hintergrund treten.

† Sämtliche Eisencarbonylhalogenide sind—entgegen der Annahme von R. J. IRVING, *loc. cit.*—typische Nichtelektrolyte mit koordinativ *sechszähligem* Metallatom, wie in früheren Arbeiten eingehend gezeigt wurde, z.B. W. HIEBER u. A. WIRSCHING *Z. anorg. Chem.* **245**, 41 (1940) u.a.

(1) 74 und 75 Mitteil.: W. HIEBER, L. SCHUSTER, und E. WEISS *Z. Anorg. Chem.* **287**, 214, 223 (1956).
(2) R. J. IRVING *J. Chem. Soc.* 2879 (1956).
(3) W. MANCHOT u. J. KÖNIG *Ber.* **57** II, 2130 (1924);
W. MANCHOT u. W. J. MANCHOT *Z. anorg. Chem.* **226**, 385 u. 389 (1936);
H. HEUSINGER, Diplomarbeit, Techn. Hochschule München (Juli 1955).
(4) W. HIEBER u. G. BADER *Z. anorg. Chem.* **190**, 193 (1930);
W. HIEBER u. H. LAGALLY *Z. anorg. Chem.* **245**, 295 (1940).
(5) W. HIEBER u. H. STALLMANN *Ber.* **75**, 1472 (1942).

dass $Ru(CO)_2J_2$ *diamagnetisch* ist. $Ru(CO)_2J_2$ ist im übrigen so beständig, dass es bisher nicht möglich war, das Kohlenoxyd durch Einwirkung chemischer Agentien abzuspalten. Im Verlauf der folgenden Untersuchungen konnte aber gezeigt werden, dass es mit Molekeln reagiert, die ein freies Elektronenpaar besitzen, wie z.B. Stickstoffbasen und Triphenylphosphin.

In Übereinstimmung mit der Beobachtung von IRVING konnten wir bestätigen, dass $Ru(CO)_2J_2$ unter scharfen Bedingungen quantitativ mit *Pyridin* reagiert. Hierbei bildet sich das orangefarbene *Dijodo-dicarbonyl-dipyridin-Ruthenium(II)*, $Ru(CO)_2(C_5H_5N)_2J_2$. Infolge ihrer wenn auch nur geringen Löslichkeit eignet sich diese Substanz wesentlich besser als das völlig unlösliche pyridinfreie Carbonyljodid zu weiteren Umsetzungen und wurde daher, insbesondere bei Reaktionen mit empfindlicheren Substituenten als Ausgangsmaterial herangezogen. Mit dem stark komplexbildenden *o-Phenanthrolin* wurde so die entsprechende orangefarbene, gegenüber der Pyridinverbindung bemerkenswerterweise etwas hellere *o*-Phenanthrolinverbindung $Ru(C_{12}H_8N_2)(CO)_2J_2$ erhalten. Die grosse Beständigkeit der Komplexe mit aromatischen Stickstoffbasen ist wohl im Auftreten einer *mesomeren Doppelbindungsstruktur* begründet:

Demgegenüber sind Verbindungen desselben Typs mit *Ammoniak* und *Äthylendiamin* insbesondere in Lösung *instabil*. So bildet $Ru(CO)_2J_2$ mit flüssigem Ammoniak oder abs. Äthylendiamin stark gefärbte Lösungen der betr. Additionsprodukte; die Diamminverbindung $Ru(CO)_2(NH_3)_2J_2$ wurde von IRVING beschrieben. Oberhalb $-30°$ (NH_3-Verbindung) bzw. $+20°$ (Äthylendiaminverbindung) zersetzen sich diese Lösungen unter Entfärbung. Da hierbei kein CO frei wird, muss eine *Carbonylierungsreaktion* mit den im Überschuß anwesenden Stickstoffbasen eingetreten sein, z.B.

Durch Nebenreaktion entsteht noch etwas kolloidales Rutheniummetall. Das nach dem Reaktionsschema erhaltene Endprodukt ist eine salzartige, in Wasser gut lösliche Verbindung mit dem exakten Molverhältnis Ru/2J. Die gefundenen Kohlenstoff- und Stickstoffwerte dagegen variieren, d.h. das durch Carbonylierung gebildete Formamid ist nicht in einem genau stöchiometrischen Verhältnis eingebaut. Wie besondere Versuche ergaben, kann Formamid tatsächlich auch sonst als Komplexligand auftreten. Sekundäre Reaktionen dieser Art erklären zugleich die beobachtete Zunahme der Leitfähigkeit solcher Lösungen.

Analog entsteht mit *Äthylendiamin* im Überschuß eine braungelbe Lösung des Addukts, die sich aber bei Zimmertemperatur unter Entfärbung zersetzt; Kohlenoxyd wird dabei nicht frei. Nach Abdunsten des überschüssigen Äthylendiamins hinterbleibt unter partieller Abscheidung von Rutheniummetall eine jedenfalls nach der primär erfolgten Carbonylierung[1] des Diamins infolge Polymerisation gebildete farblose, zähe Masse, die unter Luftabschluß zu einem farblosen Glas erstarrt.

Die Anschauung, dass speziell Liganden, die mittels eines mesomeren Doppelbindungsanteils mit dem Metallatom verbunden werden können, mit $Ru(CO)_2J_2$

stabile Anlagerungsverbindungen geben, wird weiterhin durch die Reaktion mit *Triphenylphosphin* gestützt. Dasselbe geht, ähnlich wie Pyridin, ohne CO-Abspaltung eine Additionsreaktion ein unter Bildung von *Dijodo-dicarbonyl-bis-[triphenylphosphin]-Ruthenium(II)* $Ru(CO)_2(P(C_6H_5)_3)_2J_2$. Die in gelbbraunen, rautenförmigen Kristallen anfallende Verbindung entsteht sowohl durch Substitution bei Einwirkung des Phosphins auf die alkoholische Lösung der Dipyridinverbindung wie auch unter entsprechend energischeren Bedingungen durch unmittelbare Addition des Phosphins an das Carbonyljodid in abs. alkoholischer Suspension. Die Substitutionsreaktion der Pyridinverbindung mit Triphenylphosphin verläuft wie bei allen derartigen Reaktionen zunächst nur bis zu einem Gleichgewicht; erst die erneute Umsetzung dieses Rohproduktes mit Triphenylphosphin führt schließlich zur reinen Bis-[triphenylphosphin]-Verbindung.

Zu analog gebauten, sehr stabilen Verbindungen gelangt man durch Umsetzen von Rutheniumcarbonyljodid mit *Triphenylarsin* und *Triphenylstibin*. Die Löslichkeit der Substanzen in unpolaren Mitteln wie Benzol, sowie ihre Farbe sind abgestuft:

$Ru(CO)_2(P(C_6H_5)_3)_2J_2$	$Ru(CO)_2(As(C_6H_5)_3)_2J_2$	$Ru(CO)_2(Sb(C_6H_5)_3)_2J_2$
ockerfarben	kanariengelb	kanariengelb
wenig löslich	löslich	leicht löslich

Eine ebullioskopische Molekulargewichtsbestimmung der am leichtesten löslichen Antimonverbindung in Benzol ergab deren monomere Struktur. Dies läßt den Schluß zu, dass es sich bei allen Verbindungen des Typs $RuX_2(CO)_2J_2$ um *einkernige Komplexe mit kordinativ 6-zähligem Metallatom handelt.*

Auch die Umsetzung mit *Tricyclohexylphosphin* führt zu einer analog gebauten blaßgelben, kristallinen Substanz. Ihre Löslichkeit in unpolaren Mitteln liegt zwischen derjenigen des Triphenylarsin- und Triphenylstibin-Addukts. Bemerkenswert ist indessen die Instabilität der Benzollösung dieses Komplexes, in der er teilweise wieder Tricyclohexylphosphin abspaltet, gegenüber den sehr stabilen Lösungen der analogen aromatischen Verbindungen. Hier zeigt sich wieder, dass der mesomere Doppelbindungsanteil wesentlich zur Stabilisierung beiträgt.

Die Umsetzung von Rutheniumcarbonyljodid mit *Kaliumcyanid* in abs. methanolischer Lösung führt unter geeigneten Bedingungen zum ionogen gebauten *Dikalium-dicyano-dicarbonyl-dijodo-Ruthenat(II)* $K_2[Ru(CN)_2(CO)_2J_2]$. Die Reindarstellung dieser Verbindung gelingt nur bei Verwendung von weniger als 2 Mol KCN/Ru, da sich eine Abtrennung des Anions von nicht umgesetztem Kaliumcyanid als unmöglich erwies. Leitfähigkeitsmessungen in Dimethylformamid ergaben einwandfrei den *Elektrolytcharakter* des Dicyano-komplexes, zum Unterschied von anderen Vertretern des Types $RuX_2(CO)_2J_2$:

	$t°$	Verdünnung v[$\mathscr{L}$/Mol]	Spezifische Leitfähigkeit $\varkappa[\Omega^{-1}\,cm^{-1}]$	Molare Leitfähigkeit $\mu[\Omega^{-1}\,cm^2]$
$Ru(CO)_2(C_5H_5N)_2J_2$	20	724	$2{,}723 \cdot 10^{-6}$	1,97
$Ru(CO)_2(P(C_6H_5)_3)_2J_2$	20	950	$5{,}308 \cdot 10^{-6}$	4,85
$K_2[Ru(CO)_2(CN)_2J_2]$	20	676	$2{,}583 \cdot 10^{-4}$	174

Kennzeichnend ist schließlich das Verhalten des $Ru(CO)_2J_2$ gegenüber *Isonitrilen*. Nach den bisherigen Erfahrungen kommt für die Umsetzung nur ein stark komplexbildendes, aromatisches Isonitril in Frage. Phenylisonitril scheidet wegen seines grossen Polymerisationsbestrebens, zumal bei höherer Temperatur, aus. Es wurde daher das relativ beständige p-*Anisylisonitril* herangezogen. Lässt man dasselbe auf $Ru(CO)_2(C_5H_5N)_2J_2$ in Benzol, in dem die Verbindung teilweise löslich ist, im geschlossenen System einwirken, so erfolgt zum Unterschied von den beschriebenen Reaktionen mit Triphenylphosphin und mit Stickstoffbasen keine einfache Anlagerung, sondern es findet Entbindung von Kohlenoxyd statt. Wie bei anderen Reaktionen von Isonitrilen mit Metallcarbonylen[6] tritt hierbei offensichtlich eine Substitution ein. Aus dem Reaktionsgemisch lässt sich schließlich eine zitronengelbe Substanz isolieren, die noch Kristallbenzol enthält. Unter verschiedenen Reaktionsbedingungen kristallisiert stets dieselbe, wohldefinierte Substanz der Zusammensetzung

$$Ru(CN{-}C_6H_4{-}OCH_3)_4J_2{\cdot}4/3C_6H_6,$$

vermutlich eine *Clathrate*-Verbindung. Dieselbe entsteht grundsätzlich auch, wenngleich schwieriger und in nur geringer Ausbeute, unmittelbar bei der Reaktion einer Suspension von $Ru(CO)_2J_2$ in Benzol mit *p*-Anisylisonitril; auch hierbei fällt dasselbe Produkt mit 4/3 Mol C_6H_6/Ru an. Die reine benzolfreie Tetraisonitrilverbindung erhält man schließlich beim Umkristallisieren aus Aceton, zunächst im allgemeinen nur als gelbes Öl. Die Kristallisation erfolgt bemerkenswerterweise zum Unterschied von der benzolhaltigen Substanz nur schwierig.

Die Tetraisonitril-dijodo-Verbindung, der sich das neuerdings von L. MALATESTA[7] dargestellte Chlorid und Bromid anschließt, ist als normal gebauter, einkerniger Komplex mit der Koordinationszahl 6 des Metallatoms anzusprechen und unterscheidet sich damit grundsätzlich von dem polymeren $Ru(CO)_2J_2$. Es war überhaupt nicht möglich, CO-haltige Isonitrilcarbonyle des Rutheniums zu isolieren, zum Unterschied von isonitrilhaltigen Eisencarbonyljodiden, von denen die Übergangsformen mit 1–3 Mol CO/Fe bekannt geworden sind.[6] Auch bei Einwirkung von nur 2 Mol *p*-Anisylisonitril auf die Dicarbonylverbindung entsteht nur das CO-freie Tetraisonitriljodid neben noch nicht umgesetzter Dicarbonylverbindung. So existiert jedenfalls nur *ein* isonitrilhaltiger Verbindungstyp von Ruthenium-halogeniden, wie auch von den Carbonyl-halogeniden dieses Metalls nur *ein* Bautyp vorherrscht.

VERSUCHE

1. *Einwirkung von N-Basen auf Rutheniumcarbonyljodid*

(*a*) *Dijodo-dicarbonyl-dipyridin-Ruthenium(II)*. Die als Ausgangsmaterial für die beschriebenen Komplexe häufig verwendete Dicarbonyl-dipyridin-Verbindung wird zweckmäßig durch 10-stündiges Erhitzen von 0,5 g Rutheniumcarbonyljodid[3] und 5 ml abs. Pyridin auf 120° im Einschmelzrohr dargestellt. Die weitere Aufarbeitung und Reinigung der Substanz erfolgte nach den Angaben von IRVING[8]. Sie ist diamagnetisch: $\chi_{mol} = -197 \cdot 10^{-6}$ bei 296° K und bei 77° K.

(*b*) *Dijodo-dicarbonyl-o-Phenanthrolin-Ruthenium(II)*. Etwa 0,5 g $Ru(CO)_2(C_5H_5N)_2J_2$ wurden im Einschmelzrohr mit einer Lösung von 0,75 g wasserfreiem *o*-Phenanthrolin in 25 ml abs. Alkohol 8 Std. auf siedendem Wasserbad erhitzt. Zur Reindarstellung muss das Rohprodukt erneut mit 200 mg *o*-Phenanthrolin umgesetzt werden. Zur Entfernung überschüssigen *o*-Phenanthrolins wurde mit abs.

[6] W. HIEBER u. D. v. PIGENOT *Ber.* **89**, 193, 610, 616 (1956).
[7] L. MALATESTA *Gazz. Chim. Ital.* **85**, 1111 (1955).

Alkohol, schließlich mit Äther gewaschen und im Hochvakuum getrocknet. Orangegelbe, säulenförmige Kristalle, die in Alkohol und Benzol schwer löslich, in Äther unlöslich sind. Die Substanz ist diamagnetisch.

$Ru(CO)_2(C_{12}H_8N_2)J_2$ ber. Ru 17,41; J 42,61; N 4,72; C 28,57; H 1,58;
gef. 17,19; 42,85; 4,74; 28,43; 1,36.

(*c*) *Umsetzung von $Ru(CO)_2J_2$ mit flüssigem Ammoniak und Äthylendiamin.* Die bereits von IRVING gemachten Beobachtungen über die Einwirkung von flüssigem Ammoniak auf $Ru(CO)_2J_2$, die ohne CO-Entwicklung verläuft, konnten wir bestätigen.

Kondensiert man 2 ml über Natrium dest. Äthylendiamin auf 0,3–0,4 g $Ru(CO)_2J_2$, so beobachtet man beim Auftauen eine Reaktion unter Braunrotfärbung der Lösung ohne CO-Entwicklung. Das primär gebildete Addukt zersetzt sich aber bereits bei Zimmertemperatur. Destilliert man überschüssiges Äthylendiamin ab, so hinterbleibt ein farbloser, glasiger Rückstand vermischt mit einer geringen Menge Rutheniummetall.

2. *Versuche mit Verbindungen des dreiwertigen Phosphors und seiner Homologen*

(*a*) *Dijodo-dicarbonyl-bis-[triphenylphosphin]-Ruthenium(II).* 450 mg $Ru(CO)_2(C_5H_5N)_2J_2$ wurden im Einschmelzrohr mit einer alkoholischen Lösung von 1 g Triphenylphosphin auf dem siedenden Wasserbad 10 Std. erwärmt. Zur Reindarstellung der Verbindung muss das zunächst anfallende Rohprodukt nochmals mit 500 mg Triphenylphosphin umgesetzt und mit Äther gewaschen werden. Rautenförmige, ockerfarbene Kristalle, die in Alkohol und Benzol beschränkt löslich, in Äther und Petroläther unlöslich sind.

Dieselbe Verbindung erhält man auch aus $Ru(CO)_2J_2$; 250 mg desselben wurden mit einer alkoholischen Lösung von 300 mg Triphenylphosphin im Einschmelzrohr 12 Std. auf 130° erwärmt. Das Rohprodukt wurde durch Extraktion mit abs. Alkohol gereinigt, abfiltriert und im Vakuum getrocknet. Die Substanz fällt nicht so rein an wie bei der vorher beschriebenen Darstellung.

$Ru(P(C_6H_5)_3)_2(CO)_2J_2$ ber. Ru 10,86; P 6,62; C 48,71; H 3,22;
gef. 10,92; 6,52; 48,74; 3,43.

(*b*) *Dijodo-dicarbonyl-bis-[triphenylarsin]-Ruthenium(II).* 200 mg $Ru(CO)_2J_2$ wurden mit einer alkoholischen Lösung von 650 mg Triphenylarsin im Einschmelzrohr 12 Std. auf 120° erwärmt. Das Rohprodukt wurde zur Reinigung mit Benzol extrahiert, der Extrakt mit Äther versetzt und die erhaltene Verbindung nach dem Absaugen mit Äther nachgewaschen. Kanariengelbe, in Benzol teilweise lösliche Kristalle.

$Ru(CO)_2(As(C_6H_5)_3)_2J_2$ ber. Ru 9,92; J 24,77; C 44,53; H 2,95;
gef. 10,11; 24,92; 44,31; 3,23.

(*c*) *Dijodo-dicarbonyl-bis-[triphenylstibin]-Ruthenium(II).* 150 mg $Ru(CO)_2J_2$ wurden mit einer Lösung von 500 mg Triphenylstibin in 20 ml abs. Benzol im Einschmelzrohr 15 Std. auf 110° erwärmt. Aus dem Filtrat der Reaktionslösung wird die Verbindung mit Äther gefällt und nach dem Absaugen mit Äther nachgewaschen. Kanariengelbe, in Benzol gut lösliche Kristalle.

$Ru(CO)_2(Sb(C_6H_5)_3)_2J_2$ ber. Ru 9,10; J 22,71; C 40,89; H 2,71;
gef. 9,31; 22,79; 40,62; 2,93.
Molgew. (ebullioskop.) 27,1 mg Sbst. in 3,502 g Benzol: $\Delta t = 0{,}019°$.
ber. 1117; gef. 1032.

(*d*) *Dijodo-dicarbonyl-bis-[tricyclohexylphosphin]-Ruthenium(II).* 150 mg $Ru(CO)_2J_2$ wurden im Einschmelzrohr mit einer benzolischen Lösung von 500 mg Tricyclohexylphosphin 16 Std. auf 110° erwärmt. Die Lösung wurde filtriert und die Substanz aus dem Filtrat mit Äther gefällt. Zur Reinigung musste in Benzol, dem 100 mg Tricyclohexylphosphin zugesetzt waren, umkristallisiert werden. Die mit Äther gewaschene, blaßgelbe Verbindung ist in Benzol gut löslich, in Äther und Petroläther unlöslich.

$Ru(CO)_2(P(C_6H_{11})_3)_2J_2$ ber. Ru 10,48; J 26,08; P 6,37; C 46,90; H 6,84;
gef. 10,58; 26,21; 6,43; 47,01; 6,73.

3. *Dikalium-dicarbonyl-dicyano-dijodo-ruthenat(II)*

439 mg $Ru(CO)_2J_2$ (1,07 mMol) wurden mit einer Lösung von 125 mg Kaliumcyanid (1,92 mMol) in 25 ml abs. Methanol in einem Einschmelzrohr 10 Std. auf 70° errvärmt. Von überschüssigem

$Ru(CO)_2J_2$ wird durch Extraktion mit Methanol abgetrennt. Nach Abdampfen des Lösungsmittels erhält man eine hellbraune, mikrokristalline, in Alkohol und Wasser lösliche Substanz.

$K_2[Ru(CO)_2(CN)_2J_2]$ ber. K 14,44; J 46,75; N 5,17; C 8,88;
gef. 14,30; 46,82; 5,06; 8,96.

4. *Einwirkung von* p-*Anisylisonitril auf Ruthenium(II)-carbonyl-jodide*

(*a*) *Versuche mit* $Ru(CO)_3(C_8H_8N)_2J_2$. 400 mg $Ru(CO)_3(C_8H_8N)_2J_2$ wurden mit insgesamt 900 mg in Benzol gelöstem *p*-Anisylisonitril 30 Std. auf 80° erwärmt. Die Zugabe des Isonitrils erfolgte, um Verunreinigung durch Polymerisationsprodukte möglichst zu vermeiden, unter Ausschluß des Luftsauerstoffs in 3 gleichen Teilen im Abstand von je 10 Std. Die Reaktionslösung wurde in ein Schlenkrohr überführt und durch Ätherzusatz ein braungelber Niederschlag gefällt, der mit Äther nachgewaschen wurde. Das so erhaltene Rohprodukt musste noch dreimal aus Benzol-Äther umkristallisiert werden. Die gebildete zitronengelbe, kristalline Substanz stellt eine einheitliche Verbindung dar, die 4/3 Mol Kristallbenzol/Ru enthält.

$RuJ_2(CN\text{–}C_6H_4\text{–}OCH_3)_4 \cdot 4/3C_6H_6$

ber. Ru 10,67; J 25,60; N 5,44; C 47,75; H 4,77;
gef. 10,32; 25,62; 5,65; 48,40; 3,66.

Die benzolfreie Verbindung erhält man aus der beschriebenen Substanz durch mehrmaliges Umkristallisieren aus Aceton-Äther. Hierbei scheidet sie sich zuerst als Öl ab, das bei Ausschluß jeglicher Verunreinigung nach mehrstündigem Stehen erstarrt. Die Verbindung ist diamagnetisch: $\chi_{mol} = -329 \cdot 10^{-6}$ bei 290° K und bei 17° K.

$Ru(CN\text{–}C_6H_4\text{–}OCH_3)_4J_2$ ber. Ru 11,46; J 28,55; C 43,35; H 3,17; N 6,32
gef. 11,52; 28,41; 43,38; 3,35; 6,38.

Molgew. (ebullioskop.) 32,2 mg Sbst. in 3,54 g Benzol: $\Delta t = 0{,}029°$.
ber. 888; gef. 832.

(*b*) *Versuche mit Rutheniumcarbonyljodid.* 650 mg $Ru(CO)_3J_2$ wurden wie oben mit insgesamt 800 mg *p*-Anisylisonitril, zugegeben in 3 Teilen, in benzolischer Lösung 24 Std. auf 80 bis 90° erwärmt. Nach Versetzen mit Äther schied sich ein braunes Öl ab, das durch Zusatz eines Impfkristalls zur Kristallisation gebracht werden konnte. Nach mehrmaligem Umkristallisieren aus Benzol-Äther erhielt man die kristallbenzolhaltige Isonitrilverbindung.

Bei genügend langer Umsetzungsdauer (50 Std.) und Verwendung eines grossen Überschusses an Isonitril (11,2 Mol/Ru) ließ sich das Kohlenoxyd quantitativ feststellen (gef. 1,99 Mol CO/Ru); das entstandene Reaktionsprodukt konnte hierbei allerdings infolge Verunreinigung durch Polymerisationsprodukte des Isonitrils nicht mehr kristallin erhalten werden.

Die Untersuchungen, speziell auf dem Gebiet der Kohlenoxydkomplexe der Edelmetalle, das weitgehend von uns erschlossen wurde, werden in jeder Hinsicht, vor allem auch von strukturchemischen Gesichtspunkten aus, weiter ausgebaut.

Der *Deutschen Forschungsgemeinschaft* und dem *Verband der chemischen Industrie* "*Fonds der Chemie*," danken wir für die Unterstützung unserer Arbeiten.

J. Inorg. Nucl. Chem., 1957, Vol. 4, pp. 185 to 186. Pergamon Press Ltd., London

THE EXCHANGE OF SULPHUR ATOMS IN POLYSULPHIDES

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(*Received* 3 *October* 1956)

Abstract—Certain exchange reactions of sulphur compounds, especially that between sulphide and polysulphide, have been re-examined.

RESULTS obtained in the study of the hydrolysis of sulphur and of polysulphides made it seem desirable to reinvestigate the exchange of polysulphide-sulphur with sulphide-sulphur.

Our earlier work[1] had shown that, on heating, polysulphide-sulphur hydrolyses forming hydrogen sulphide and thiosulphate, e.g.

$$S_5^{2-} + 3H_2O \longrightarrow 3H_2S + S_2O_3^{2-} \qquad (1)$$

In consequence of this there is no guarantee that earlier exchange studies,[2–4] which were performed with polysulphides prepared by prolonged heating of a solution of sodium sulphide and sulphur, and which seemed to indicate a total exchange of the sulphur atoms, reveal the correct mechanism of the process. Because of the hydrolysis indicated in equation (1) a part of the polysulphide-sulphur changes to sulphide-sulphur without any exchange. Besides, some error may also be caused by the fact that the sulphur, which precipitates when the polysulphide is decomposed by hydrochloric acid, hydrolyses on boiling and forms active hydrogen sulphide without exchange. Finally, we had to check the suggestion of HAISSINSKY and PESCHANSKY,[4] who considered the possibility that the precipitating sulphur might have a catalytic effect on the exchange reaction. It must be mentioned that GURJANOVA, SIRKIN, and KUZINA[5] do not agree with this idea.

The elementary sulphur used in our experiments was prepared from S^{35}-labelled sodium sulphate as follows:

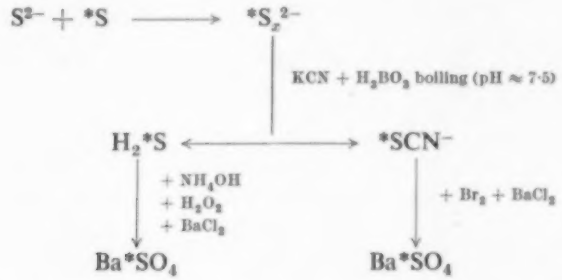
$$SO_4^{2-} \xrightarrow{BaCl_2} BaSO_4 \xrightarrow[900–950°]{H_2} BaS \xrightarrow[\text{(absorbed in NaOH)}]{HCl} H_2S \xrightarrow{I_2 + HCl} S$$

The sulphur was coagulated by means of lanthanum nitrate solution and recrystallized from benzene.

Because of the arguments mentioned above, the polysulphide was prepared from labelled sulphur and sodium sulphide at room temperature in an oxygen-free medium

[1] E. SCHULEK, E. KÖRÖS, and L. MAROS *Magy. Tud. Akad. Kém. Oszt. Közl.* **7**, 91 (1955); *Acta Chim. Hung.* **10**, 291 (1956).
[2] H. H. VOGE and W. F. LIBBY *J. Amer. Chem. Soc.* **59**, 2474 (1937).
[3] H. H. VOGE *J. Amer. Chem. Soc.* **61**, 1032 (1939)
[4] M. M. HAISSINSKY and D. PESCHANSKY *J. Chim. Phys.* **47**, 191 (1950).
[5] E. N. GURJANOVA, J. K. SIRKIN, and L. S. KUZINA *Dokl. Akad. Nauk SSSR* **86**, 107 (1952).

in a suitable micro-apparatus. For the separation of polysulphide-sulphur and sulphide-sulphur, potassium cyanide and boric acid were used:[6]



The activity of the barium sulphate precipitates was measured with a GM flow counter. Corrections were applied for self-absorption. In every run, total exchange was found.

In the course of the separation method outlined above, on the one hand the sulphide and the thiocyanate are together in the same solution for a while, and on the other hand the sulphide may be oxidized to thiosulphate by traces of oxygen. It seemed therefore necessary to examine the exchange of sulphur atoms between sulphide and thiocyanate* and between thiocyanate and thiosulphate. In each case the thiocyanate was labelled. In 1 hour at pH ≈ 7·5 no exchange was found.

The exchange was also studied in the solid phase. Labelled sulphur was dissolved in pure toluene and allowed to react with dehydrated sodium sulphide. The sodium polysulphide formed in this way was decomposed with concentrated phosphoric acid and the hydrogen sulphide obtained was converted to barium sulphate. This precipitate was found to be active.

Some questions concerning the structure of the polysulphide ion, which might explain the exchange, and especially concerning the equivalence of its sulphur atoms, remain to be dealt with at a later date.

* This exchange reaction was studied under different conditions by HEISIG and HOLT [7] and no exchange was found.

[6] E. SCHULEK *Z. Anal. Chem.* **65**, 352 (1924/25).

[7] G. B. HEISIG and R. HOLT *J. Amer. Chem. Soc.* **74**, 1597 (1952).

J. Inorg. Nucl. Chem., 1957, Vol. 4, pp. 187 to 204. Pergamon Press Ltd., London

FACTORS AFFECTING THE SOLUTION OF INORGANIC SALTS IN ORGANIC SOLVENTS*

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(*Received* 29 *November* 1956)

Abstract—Inorganic salts are appreciably soluble in organic media, principally of the oxygenated forms (alcohols, ketones, ethers, esters), when they are capable of forming neutral molecules in solution. This property is largely confined to the transition elements. Those of the first long series, and in the trans-radium region, accomplish this without forming undebatably covalent compounds; other subgroup elements which are solvent-soluble show a stronger tendency toward covalent bond formation, and may show solubility in chlorinated hydrocarbons and benzenoid solvents in which the first group mentioned are not usually soluble. The salts of the first three groups of the periodic table generally are not organic-soluble, because their co-ordinative power is relatively low, and their solid lattice energies are high. They tend strongly to approach the point-charge characterization on which the electrostatic approach to aqueous solution chemistry is based.

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IT is a widely accepted dogma that the "natural" solvent for inorganic salts is water. With the crystallographic demonstration of the intrinsically ionic nature of such salts, and given the almost uniquely high dielectric constant for water, strong arguments can be presented to back this principle. As a corollary, one then obtains the statement that organic liquids of low dielectric constant (in comparison with water) and markedly dissimilar to water (i.e. other than small hydroxyl-bearing molecules miscible with water) are poor or completely negligible solvents for such ionic salts. Essentially nonionic salts, of which there are some examples, are of course excluded from consideration.

An example of a typical relationship is that for the system KCl—water—ethanol,[1] shown in Fig. 1. Even with the low-weight hydroxylic solvent, which is miscible with water, the salt solubility is very low, and in the composition region between the two pure liquid components, the solubility is continually depressed by addition of organic component. With a nonhydroxylic organic component such as acetone[2] (Fig. 2), the difference between solubility in the organic phase and in water is so great that the normally miscible liquids are separated into two phases, an acetone-rich phase of low salt content and a water-rich phase of higher salt content.

If the salt is much more soluble, as for example potassium fluoride is, a separation into two liquid phases can be obtained even for the ethanol-water system[3] (Fig. 3). The difference between hydroxylic and nonhydroxylic organic components becomes more marked with such a highly soluble salt. Division into two liquids occurs more readily with acetone than with ethanol[4] (Fig. 4), and the acetone-rich phase is not only very largely salt-free, but almost anhydrous also.

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

(1) R. FLATT and A. JORDAN *Helv. Chim. Acta* **16**, 37 (1933); G. W. FERNER and M. G. MELLON *Ind. Eng. Chem.* Anal. Ed. **6**, 345 (1934).
(2) W. HERZ and KNOCH *Z. anorg. Chem.* **41**, 319 (1904).
(3) G. B. FRANKFORTER and F. C. FRARY *J. Phys. Chem.* **17**, 402 (1913).
(4) G. B. FRANKFORTER and L. COHEN *J. Amer. Chem. Soc.* **36**, 1103 (1914).

Examples of this sort of behaviour, with different salts and different organic components, could be multiplied almost without limit. A considerable collection of them, differing only in the quantitative relations from the examples given here, may be found in a compilation by A. W. FRANCIS.[5]

Not only the usual inorganic salts show a decreased solubility with organic solvents. The amino acid glycine, for example, is very soluble in water. Like all

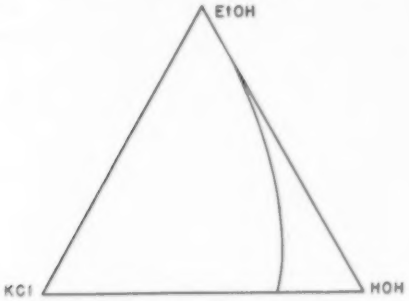

FIG. 1.—The system KCl—H_2O—ethanol.

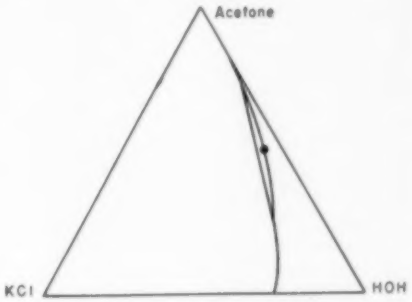

FIG. 2.—The system KCl—H_2O—acetone.

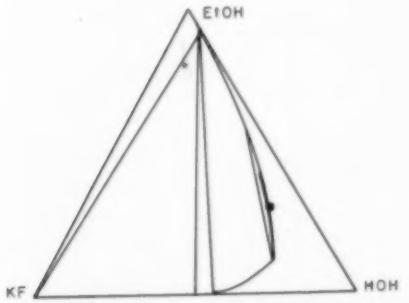

FIG. 3.—The system KF—H_2O—ethanol.

FIG. 4.—The system KF—H_2O—acetone.

amino acids, it probably exists to some extent in the zwitterion form, $^{+}H_3NCH_2—COO^{-}$. Probably as a consequence of this, addition of methanol to the aqueous solution is a standard technique for obtaining almost quantitative crystallization of the amino acid.

One may proceed to another system, $CoCl_2$—water—*t*-butyl alcohol.[6] From the melting-point of the alcohol (about 25°C) up, the two liquids are miscible. The phase diagram at 25° (Fig. 5) shows a very short liquid section, as alcohol is added to the aqueous system, before separation into two liquid phases takes place, as in other systems we have seen. At the higher alcohol end, the salt solubility drops to very low values, again in familiar form. As the region of approximately 95% alcohol is passed, however, there is an unusual *upturn* in the salt solubility curve,

[5] A. W. FRANCIS in A. SEIDELL and W. F. LINKE *Solubilities of Inorganic and Organic Compounds* pp. 823ff. Supplement to the 3rd Ed. D. Van Nostrand, New York (1952).
[6] L. I. KATZIN and J. R. FERRARO *J. Amer. Chem. Soc.* **75**, 3825 (1953).

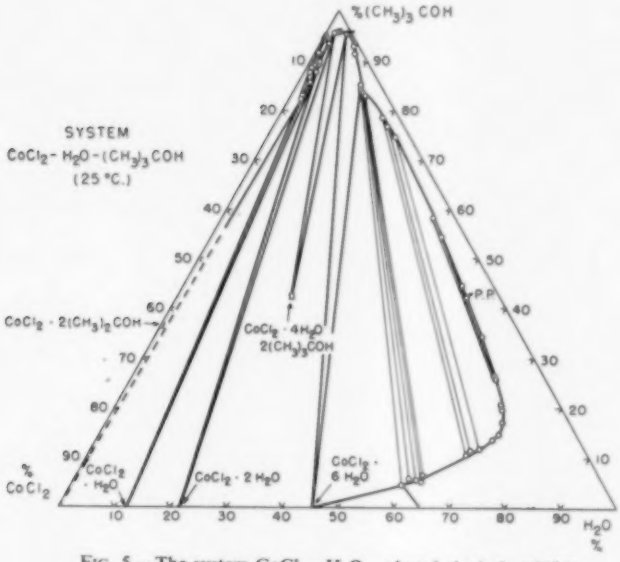

FIG. 5.—The system $CoCl_2$—H_2O—*t*-butyl alcohol at 25°C.

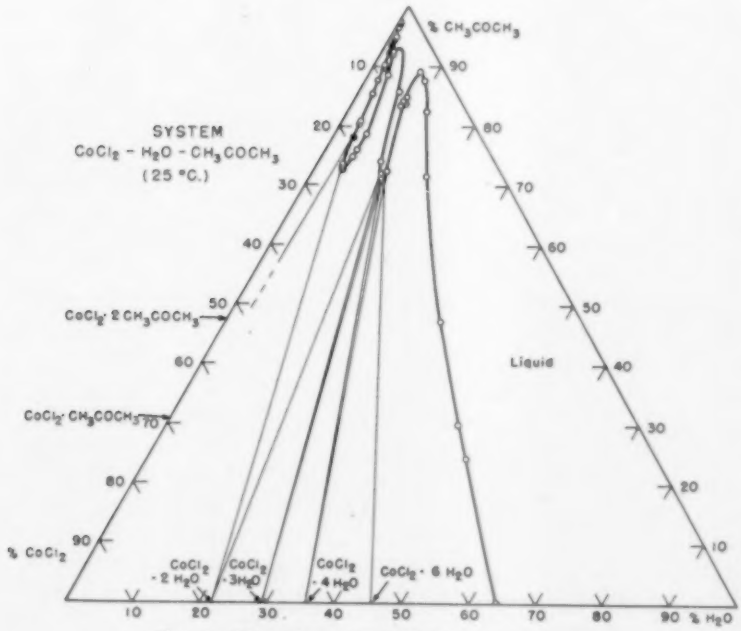

FIG. 6.—The system $CoCl_2$—H_2O—acetone at 25°C.

and with it, in the water content of the liquid phase, to peak salt concentration of about 15·4%. From this peak the salt solubility drops toward the low value characteristic of the anhydrous $CoCl_2$—*t*-butyl alcohol system.

The $CoCl_2$—water—acetone system[7] (Fig. 6) is perhaps more startling. The salt solubility drops somewhat reluctantly with added organic content, finds a minimum at about 90% acetone which is higher than the analogous point in the *t*-butyl alcohol system, and then turns up, in a similar fashion to the alcohol system.

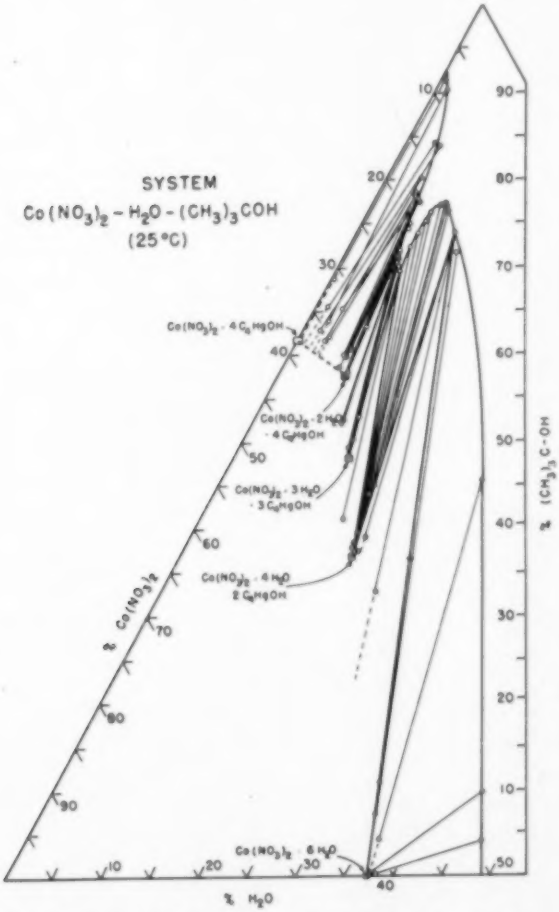

FIG. 7.—The system $Co(NO_3)_2$—H_2O—*t*-butyl alcohol at 25°C.

The salt solubility is higher in this upturn than for the alcohol, and after the drop from this peak commences and continues for a space, there is a *second* upturn which carries to an even higher salt solubility than the first, before the drop-off to the low value of the anhydrous system takes place again.

If one uses cobaltous nitrate[8] rather than the chloride, as in Fig. 7, addition of

[7] L. I. KATZIN and J. R. FERRARO *J. Amer. Chem. Soc.* **74**, 2752 (1952).
[8] L. I. KATZIN and J. R. FERRARO *J. Amer. Chem. Soc.* **72**, 5451 (1950).

t-butyl alcohol has a relatively minor depressive effect on the salt solubility, and at higher alcohol concentrations the by now familiar sharp upturn in salt solubility is seen again. If instead of *t*-butyl alcohol the organic component is acetone (Fig. 8), one is put to it to be certain that any depression of the salt solubility is seen, and in fact at the maximum which appears again at higher acetone concentrations, the mass concentration of salt in the solution is higher than in pure water.

With these cobalt salts, to summarize, we have to reconcile ourselves to several phenomena "atypical" of salt behaviour as it has been outlined above. First is the fact that though the salt solubility may drop initially with increased concentration of organic component, there is a high-solubility region (or two, with $CoCl_2$—water—

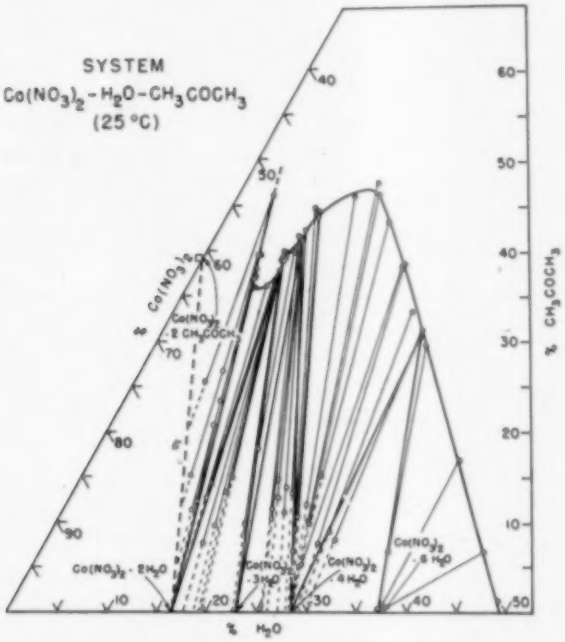

FIG. 8.—The system $Co(NO_3)_2$—H_2O—acetone at 25°C.

acetone) at high organic content. Second is the fact that the salt solubility in the high organic region, even on a weight basis, may be higher than the solubility in water. Third is the fact that for these salts the nonhydroxylic acetone appears to be a better solvent than the hydroxylic *t*-butyl alcohol. (Liquids such as hydrocarbons, chloroform, or carbon tetrachloride are not solvents for these salts.)

It should be stated clearly at this point, also, that such solubility relations are not restricted to these cobaltous salts, and that the general aspects of the phenomenon will be discussed later below.

In order to discuss the phenomena shown in the cobaltous salt series efficiently, there will first be given the explanation which the author has developed for what happens on a molecular scale, the resulting picture will be experimentally justified, and application to the gross relations will follow.

The basic concept is that, though it does not form stable complexes of the sort

characteristic of Co(III), Co(II) has a definite co-ordination number (actually, two co-ordination numbers) in the range of conditions of interest here. Starting under the conditions of aqueous solution, the co-ordination positions are filled with water groups, and the anions are somewhere in the general vicinity, somewhat constrained by electrostatic attraction. As one adds an organic liquid component, there is set up a competition between the water and organic electron donor for the co-ordination positions around the cation, leading to a degree of replacement of water by organic molecules dependent on the exact species, concentrations, relative base strengths, etc.

Another change is taking place at the same time—a lowering of dielectric constant which increases the attraction between cation and anion. If one takes the anion as nitrate, there may be a region of composition in which there is appreciable electrostatic ion-pair formation, but as high organic composition is approached, the attraction between anion and cation makes the former a sufficiently strong competitor for co-ordination position around the cobaltous ion that it enters the co-ordination sphere, and one finds a composition at which the principal species is an undissociated neutral salt molecule, with four co-ordination positions taken up by some combination of water and organic groups, depending upon exact conditions. At this point there exists essentially a solution of one neutral molecular species (solvated cobaltous nitrate) in another (the organic medium), a familiar situation. The usual criteria applied to distinguish co-ordinate from "ionic" bonding still indicate ionic relationship, of which more will be said later.

The points of this explanation for the general solubility relation which need to be demonstrated are (a) that the anion is really taken into the co-ordination sphere (b) that there is a definite co-ordination number which can be demonstrated, and (c) that the details of the rather complicated phase diagrams can be explained with the aid of this information.

The absorption spectrum of the nitrate ion between 220 and 350 millimicrons is well known, and if a salt such as lithium nitrate is dissolved in *iso*propyl or *t*-butyl alcohol, the ultra-violet absorption is very little different from that of the dilute solution in water. Cobaltous perchlorate, in the same medium, shows no absorption in the same spectral region. Addition of lithium nitrate to the cobaltous perchlorate produces a spectrum, very markedly altered and intensified, but still recognizable as originating with the nitrate group[9,10] (Fig. 9). Similarly, in the visible region, with this organic solvent and others, the absorption spectrum of cobaltous perchlorate is very like that of the aqueous solution, but addition of nitrate produces a marked intensification and shift of the spectrum[10,11] (Fig. 10). Such significant electronic alterations imply much more intimate relations between the electron clouds of the two groups than would be expected for simple electrostatic pairing between an anion and a fully solvated cation. The conclusion seems unavoidable that there is direct contact and electron sharing or other interaction between cation and anion—i.e. the latter has entered the co-ordination sphere. One may add that the same sort of conclusion, from absorption spectral evidence, is reached for the halide ions, and for thiocyanate ion.[12,13,14]

[9] L. I. KATZIN *J. Chem. Phys.* **18,** 789 (1950).
[10] L. I. KATZIN and E. GEBERT *J. Amer. Chem. Soc.* **72,** 5455 (1950).
[11] L. I. KATZIN and E. GEBERT *Nature* **175,** 425 (1955).
[12] L. I. KATZIN and E. GEBERT *J. Amer. Chem. Soc.* **72,** 5464 (1950).
[13] L. I. KATZIN and E. GEBERT *J. Amer. Chem. Soc.* **72,** 5659 (1950).
[14] L. I. KATZIN *J. Chem. Phys.* **20,** 1165 (1952).

To demonstrate the co-ordination number situation, one must turn to the halides—$CoCl_2$ will be used for illustration.[12] This salt, in acetone for instance, shows a deep blue colour, which is different from that of cobaltous nitrate. Through the

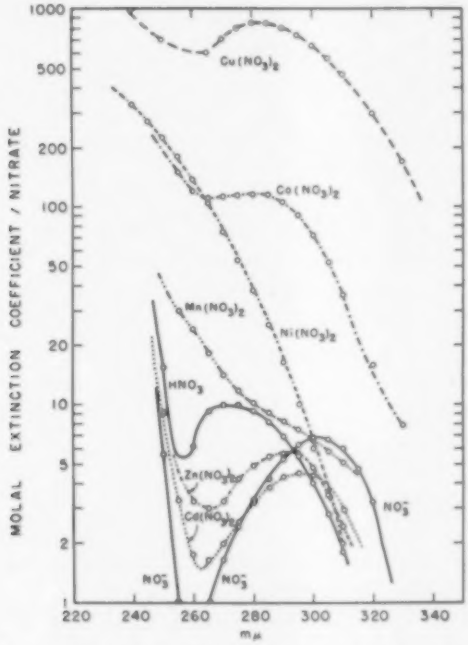

FIG. 9.—The ultra-violet absorption spectra of certain nitrates in *iso*propyl alcohol.

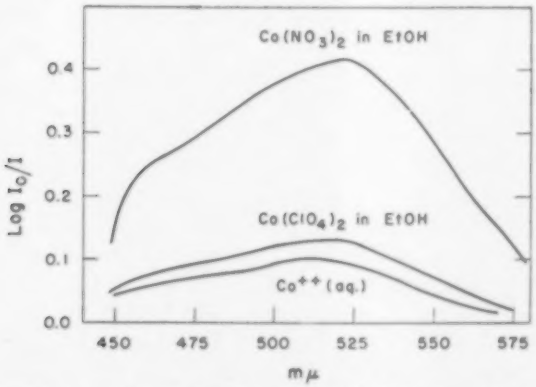

FIG. 10.—The absorption of $Co(ClO_4)_2$ and $Co(NO_3)_2$ in ethanol in the visible region.

method of continuous variations,[15,10] it is possible to show that both the red peak of cobaltous nitrate in acetone, at about 540 millimicrons, and the blue peak of cobaltous chloride in acetone, at about 575 millimicrons, are due to forms with two anions per cobalt. On making a dilute solution of hydrated $CoCl_2$ in methanol,

[15] P. Job *Ann. Chim.* [10] **9**, 113 (1928).

the principal absorption is that corresponding to the red peak of cobaltous nitrate, with a minor peak at longer wavelength. Addition of lithium chloride to the solution increases the intensity of the longer-wavelength peak and changes its identity somewhat, but the red peak is not greatly affected. This is consistent with change of only a small part of the red form to the blue form with much higher extinction coefficient. A continuous variations analysis of the spectra at both the 520- and 575-millimicron wavelengths, using mixtures of cobaltous perchlorate and lithium chloride, shows that *both* peaks involve components with two chlorides per cobalt. It is clear then that the difference between red and blue forms is one of the molecular groups attached to a $CoCl_2$ entity.

Returning to $CoCl_2$ in acetone, the characteristic blue spectrum is altered to another, also individual, blue spectrum on addition of a single equivalent of LiCl. A second equivalent produces another, incomplete change, which is complete with a third equivalent of the salt, and the spectrum is not further affected by additional LiCl. If to the $CoCl_2$ solution with a single equivalent of LiCl one adds a single equivalent of pyridine, a distinctive variant of the absorption spectrum obtained without the pyridine is obtained. If one adds the single equivalent of pyridine to the $CoCl_2$ solution with three or more equivalents of LiCl, one obtains the same spectrum as if a single equivalent of LiCl were present. The conclusion derived is that the pyridine has displaced one of the four chlorides probably present in the cobalt co-ordination sphere. Since it would be expected that a solvent group present would be more readily displaced than the chloride (which has already displayed its ability to replace solvent), there must be no such group in the co-ordination sphere when pyridine is absent, and therefore the four chlorides must have filled the co-ordination sphere. The co-ordination number must therefore be 4 for these several blue cobalt forms. This conclusion is further supported by preparing a blue salt such as Cs_3CoCl_5 or Cs_2CoCl_4, observing that the absorption spectrum of the solid is the same as for the $CoCl_4^=$ group in solution,[16] and demonstrating crystallographically that this group is present in the solid.[16,17] Blue glasses have also been shown to contain 4-co-ordinate cobalt.[18]

The several blue-coloured forms of cobaltous halide solutions are thus identified as containing 4-co-ordinate Co(II). The methanol solutions gave evidence that $CoCl_2$ solutions contained another grouping, of different and presumably higher co-ordination number, showing red colour. From the formation of hexahydrated solids, from the fact that $CoCl_2$ in pyridine shows a spectrum with both blue and red forms, while hexapyridinated solid will precipitate from concentrated solutions, and the crystallographic fact that in its solids hydrated $CoCl_2$ has 6-co-ordinate cobalt, the assumption seems reasonable that the states giving the red (pink) colour are 6-co-ordinate.

Having demonstrated that there is a definite co-ordination number or numbers, and that the anion is taken into the co-ordination sphere in organic solutions of the cobaltous salts, it remains to demonstrate that the details of a complicated ternary phase diagram, such as that of the system $CoCl_2$—water—acetone (Fig. 6) can be explained satisfactorily by this behaviour.

[16] L. I. KATZIN *J. Amer. Chem. Soc.* **76**, 3089 (1954).
[17] H. M. POWELL and A. F. WELLS *J. Chem. Soc.* **1935**, 359.
[18] W. A. WEYL *J. Appl. Phys.* **17**, 628 (1946).

The starting equilibrium solid, at the high-water end of this system, is $CoCl_2 \cdot 6H_2O$ or, as it should be written to illustrate the argument, $(Co(H_2O)_6)Cl_2$. Addition of acetone lowers the solubility, as expected, to a minimum at 90–95% acetone. (In the *t*-butyl alcohol system the lower solubility at the minimum is probably related to the ready formation of mixed hexasolvates, of low solubility.) The upturn in the solubility value as water activity is further decreased is to be equated with the first breaking into the water co-ordination shell, and the formation of the initial quantities of $(Co(H_2O)_4Cl_2)$. A straight-edge laid to pass through the composition $CoCl_2 \cdot 4H_2O$ on the base of the triangle will also comfortably follow the straight-line portion of the solubility upswing. From the geometric properties of these ternary plots, this is equivalent to saying that the points along that solubility curve are derivable by adding tetrahydrate to the saturated solution of hexahydrate in slightly wet acetone. This is what would be expected if the solubility increase is in fact largely due to the solute species indicated.

The straight-line portion of the drop from the solubility maximum likewise may be extrapolated to the baseline, and to a good approximation intersects at the composition $CoCl_2 \cdot 3H_2O$. This would be interpreted to mean that, as the water activity is lowered the solute loses water, greater and greater conversion to $(Co(H_2O)_3SCl_2)$ taking place, where *S* represents a molecule of acetone. This mixed solvate is apparently less soluble than the tetrahydrated form, giving an apparent loss of trihydrate from the liquid phase, even though the solvent molecule itself does not survive into the solid phase.

Next, accompanied by a linear portion which extrapolates to $CoCl_2 \cdot 2H_2O$, there occurs a second upturn in salt solubility. This is to be ascribed to the major change in co-ordination number, from 6 to 4, and the appearance of the solute species, $(Co(H_2O)_2Cl_2)$. With further replacement of the water by acetone, the solubility drops off steadily to the low value characteristic of the anyhdrous $CoCl_2$-acetone system.

Cobaltous nitrate, which shows only co-ordination number 6 for the cation, has only a single solubility upsweep. Further characteristic of the difference between nitrates and chlorides is the almost immediate increase of solubility with the first addition of acetone—the normally expected sharp drop is not seen. This is a fairly general phenomenon, in that nitrate 2-1 salts of the transition elements usually are more readily soluble in organic solvents than the chlorides. As the ionic radii of the anions are almost the same, and, if anything, the chloride ion is slightly more efficient as a complexing agent in aqueous solution, the explanation may involve a slightly higher lattice energy of the halides compared to the nitrates. In fact, the specific gravities of the chlorides are higher than those of the corresponding nitrate hydrates,[19,20] while the formula weights are lower, indicating closer ionic spacings.

Another difference which needs explanation is why the $CoCl_2$ system with *t*-butyl alcohol shows but a single solubility maximum, whereas the acetone system shows two, as discussed above. This seems to be a property of acetone, manifest in other ways, which for convenience may be designated as "resolving power." Comparison of the equilibrium solid phases in the $CoCl_2$ systems with alcohol and acetone as the organic components shows, as in the $Co(NO_3)_2$ instance,[8] and also with uranyl

[19] L. I. KATZIN and J. R. FERRARO *J. Amer. Chem. Soc.* **75**, 3821 (1953).
[20] L. I. KATZIN and J. R. FERRARO *J. Amer. Chem. Soc.* **74**, 6040 (1952).

nitrate,[21] that the acetone systems show sharper separation of hydrates, or show hydrates that are not visible in the *t*-butyl alcohol systems. This is to be ascribed to a quirk of the water activity-solution composition relations, due to which the acetone solutions show a much greater spread of analytical composition for a given water activity difference than is shown by the alcohol solutions. The result is that the fixed water activity (and solution composition) points corresponding to simultaneous presence of a pair of neighbouring hydrates, as the cobaltous chloride dihydrate-trihydrate and trihydrate-tetrahydrate pairs, are not analytically resolved, for the alcohol situation, and the phase diagram seems to skip a solid phase. With the organic component acetone, these solution compositions and solid phases are "resolved," and the phase diagram thus shows all the hydrates that exist, even when their stability regions, in terms of water activity, are very short. This behaviour may in turn rest on water-solvent interactions which are beyond the scope of this discussion.

There is a clear rationale to be seen for the unexpected superiority of a ketone such as acetone as solvent, over that of an alcohol. The alcohols are stronger electron donors than the ketones, as exemplified by the appearance of mixed water-alcohol hexasolvates in the systems containing *t*-butyl alcohol as the organic component (Figs. 5, 7), whereas only the simple hydrates appear in the acetone systems. Because of this strong electron donor nature, lowering the water activity to some given value fails to reduce the total solvation of the cation from 6, to allow the anions to enter the co-ordination sphere. In other words, the organic component competes strongly with the anion for the co-ordination positions, inhibiting formation of the neutral associated species which has the high solubility in the organic component. There is probably also a factor of high lattice energy for the hexasolvated salts. This influence of alcohol vs. ketone has been shown in detail in spectrophotometric studies of the Co(II)-thiocyanate complexes,[13] and is the basis for the frequent empirical observation of the analytical chemist that his colorimetric extraction procedure works better with a ketone than an alcohol as the organic phase.[22] Esters might in some cases be even better, but for the complication of potential hydrolysis.

It therefore seems justified to consider the basic propositions given above for the solubility phenomena to be well founded. Their extension to other types of phenomena is also consistent. Consider for example a two-phase solvent extraction system, rather than a single-liquid miscible system. In such a system, with oxygenated organic liquids as the nonaqueous phase, uranyl nitrate shows very favourable distribution into the organic phase. A plot of the water content of the organic phase against its uranyl nitrate content[21] for a selection of solvents is shown in Figure 11. The solvents are (I) *iso*butyl alcohol, (II) ethylene glycol diethyl ether, (III) methyl *iso*butyl ketone, (IV) diethyl ether, and (V) dihexyl ether. The major portions of the data for I, III, IV, and the second part of II are essentially linear, with slope 4·0—four moles of water per mole of uranyl nitrate, corresponding to the species $(UO_2(H_2O)_4(NO_3)_2)$ extracted. The first part of the data for II shows a slope 6·0, with an abrupt transition to 4·0, suggesting the extraction of the electrostatically associated $(UO_2(H_2O)_6^{++}(NO_3)_2^-$ at low salt concentration (high water activity). The apparent slope 2·0 for hexyl ether, based on few points, needs more investigation

[21] L. I. KATZIN and J. C. SULLIVAN *J. Phys. Chem.* **55**, 346 (1951).
[22] C. E. CROUTHAMEL and C. E. JOHNSON *Anal. Chem.* **24**, 1780 (1952).

though it suggests a possible lower co-ordination number for uranyl ion, analogous to Co(II). What is remarkable is the unexpected lengths of these linear portions with slope 4·0, as earlier onset of replacement of water by organic molecules might be expected, which would give curved lines with only initial slopes as high as 4·0. This is a special property of uranyl ion, ascribable to the difference in binding energy for the several water groups, which will be mentioned further below.

Because uranyl nitrate is so readily extracted from water, and because the water transfer per mole of salt is constant over such a long range, it is not necessary to concern oneself with small fluctuations in the free water of the organic phase, due

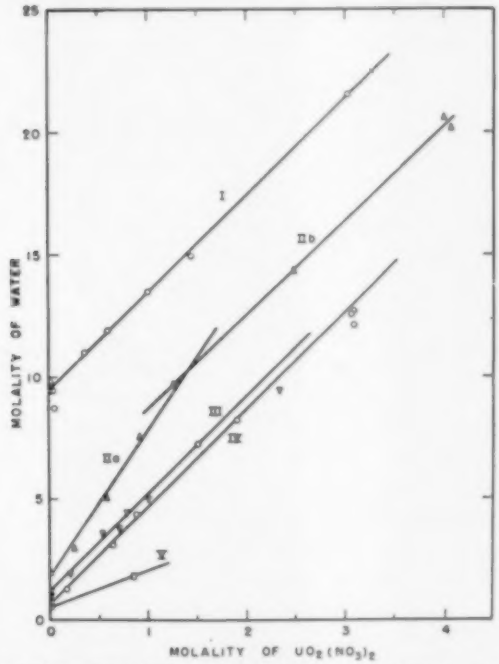

FIG. 11.—Molality of water as a function of molality of uranyl nitrate in organic phases equilibrated with aqueous uranyl nitrate. I, *iso*butyl alcohol; II, diethyl ether of ethylene glycol; III, methyl *iso*butyl ketone; IV, diethyl ether; V, hexyl ether.

to altered water activity of the aqueous phase. With more difficult extraction situations such as for the nitrates of La(III), Co(II), Mg(II), Zn(II), and Ca(II) into *n*-hexanol,[23] for example, conditions are not so favourable, and corrections need to be evaluated. A simple way is to "calibrate" a solvent by measuring the water extracted from aqueous salt solutions for which salt extraction is negligible and for which water-activity data are available. Such determinations with the solvent 2-octanol[24] have yielded slopes of water : salt plots of about 2 for $ZnCl_2$ and LiCl, about 3 for $CaCl_2$, and high values—10–15—for $Co(ClO_4)_2$ and $Ni(ClO_4)_2$. These last are most probably related to the poor ability of perchlorate ion to co-ordinate with cations, and suggest also that Co(II) may under such conditions show co-ordination numbers higher than 6. Other evidence pointing in this same direction is the composition of solid

[23] C. C. TEMPLETON and L. K. DALY *J. Amer. Chem. Soc.* **73**, 3989 (1951).
[24] P. C. YATES, R. LARAN, R. E. WILLIAMS, and T. E. MOORE *J. Amer. Chem. Soc.* **75**, 2212 (1953).

mixed pyridine-water solvates of cobaltous perchlorate,[25] in which the ratio of pyridine plus water to cobalt ranges up to 11·5. Some structural studies of these compounds would be useful. The colours of these Co(II) perchlorates also tend towards a pale orange, rather than the reddish hues of the nitrate and chloride hydrates. Interpretation of the water-salt ratios in the octanol experiments above must be tentative, since very concentrated solutions, with low water activities, were needed to achieve significant transfer to the organic phase.

Accepting the premises that neutral solute molecules are formed of cations with known integral co-ordination numbers, it becomes possible to investigate some

TABLE 1.—HEATS OF SOLUTION OF COBALTOUS NITRATE DIHYDRATE IN VARIOUS ORGANIC SOLVENTS
(kcal/mole)

Solvent	ΔH
Dimethyl formamide	−17·76
Monoethyl ether of ethylene glycol	−6·56
Diethyl ether of ethylene glycol	−4·89
Tetrahydrofuran	−4·30
Acetone	−1·65
Methyl ethyl ketone	0·30

interesting relations experimentally. For example, cobaltous nitrate shows 6-co-ordinate forms exclusively, in organic solution. If one starts with the dihydrated solid, there are only two water molecules and two anions to fill six co-ordination positions, so two molecules of solvent must be co-ordinated for each molecule of nitrate that dissolves. Measurement of the heat of solution of the dihydrate in a series of organic solvents will give a comparative measure of the energy of interaction between cation and solvent groups. A summary of some measurements of this sort[20] is shown in Table 1. As might be anticipated, the order of heats of solution is essentially that of the order of electron-donor strengths or "base-strength" of these solvents.

It is also possible to estimate an otherwise unobtainable value, such as the relative energy for putting two water groups in the vacant co-ordination positions. This is accomplished by using acetone, a relatively weak electron donor, and a small addition of water, as solvent. The water is sufficient to occupy the vacant co-ordination positions, but not enough to displace the anions from the co-ordination sphere, or to ionize the solute. Other uses of the measurements also appear. For instance, with the aid of estimates of the lattice energies (more precisely, lattice-energy differences) of the several solid solvates, it is possible to obtain not only the relative energies of binding solvent groups to a cation, but usefully reliable absolute values for the binding, not only to a given cation, but to a given co-ordination position (Table 2). This in turn makes it possible, for example, to show that the ready solvent extractability of uranyl nitrate is ascribable to the abnormally loose binding of two water molecules in the primary hydration shell.[20]

[25] L. I. KATZIN, J. R. FERRARO, and E. GEBERT *J. Amer. Chem. Soc.* **72**, 5471 (1950).

TABLE 2.—WATER-BINDING ENERGIES OF HYDRATES OF COBALTOUS NITRATE, URANYL NITRATE, AND CUPRIC NITRATE

Solid	Density	U (kcal/mole)	ΔH sol. (kcal/mole)	Transition	Water binding energy (kcal)
$Co(NO_3)_2 \cdot 6H_2O$	1·87	350·8	4·96	Hexahydrate→tetrahydrate	47·0
$Co(NO_3)_2 \cdot 4H_2O$	2·05	375·3	3·50	Tetrahydrate→trihydrate	33·6
$Co(NO_3)_2 \cdot 3H_2O$	2·24	393·9	−0·98	Trihydrate→dihydrate	32·7
$Co(NO_3)_2 \cdot 2H_2O$	2·40	411·8	−5·28	——	—
$UO_2(NO_3)_2 \cdot 6H_2O$	2·74	333·5	5·48	Hexahydrate→trihydrate	54·0
$UO_2(NO_3)_2 \cdot 3H_2O$	2·93	352·2	−1·66	Trihydrate→dihydrate	33·7
$UO_2(NO_3)_2 \cdot 2H_2O$	3·35	371·7	−5·37	——	—
$Cu(NO_3)_2 \cdot 6H_2O$	1·92	351·9	−10·71	Hexahydrate→trihydrate	68·8
$Cu(NO_3)_2 \cdot 3H_2O$	2·047	381·0	−2·5	——	—

The discussion so far has dealt largely with the 2-1 salts. Salts of the 3-1 type [Ga(III), Fe(III)] can also be brought into organic phases, but usually from concentrated HCl or other halogen acid. It has been shown[26] that the species in the organic phase is $HMCl_4$, and that one is dealing with the tetrahedral MCl_4^- group. This is another instance of the change of co-ordination number in the presence of chloride, the co-ordination number 6 being usual for Fe(III). Here the formation of the 4-co-ordinated entity seems critical for transfer to the organic phase, though the fundamental difficulty may be the acid concentrations needed to lower the water sufficiently.

The historical solvent for the 3-1 halides extraction system has been ether, and a number of studies have been made as to which ether gives the best distribution results. It has been shown,[27] however, that there is nothing critical about ether as a solvent for these systems, and as a matter of fact, in line with what has already been found with the 2-1 salts, the solvents giving extraction with the lowest acid concentrations are probably the ketones. Here again a factor of co-ordination position competition makes itself felt, and the ketones, much weaker electron donors than alcohols or ethers, would be expected to facilitate formation of the MX_4^- complex.

The principal water-stable 4-1 salt, thorium nitrate, though much less readily extracted from aqueous solution than is uranyl nitrate, is quite soluble in organic liquids of the oxygenated type. This salt has been studied by the technique of following the composition of the organic phase, saturated with thorium nitrate in the presence of saturated aqueous thorium nitrate.[28] Under these conditions, the activity both of water and of thorium nitrate is closely fixed, and it becomes possible to compare compositions of different organic phases, and mixtures of an

[26] S. KATO and R. ISHII *Sci. Papers Inst. Phys. Chem. Research* Tokyo **36**, 82 (1939); J. AXELROD and E. H. SWIFT *J. Amer. Chem. Soc.* **62**, 33 (1940); N. H. NACHTRIEB and J. G. CONWAY *ibid.* **70**, 3547 (1948); R. J. MYERS, D. E. METZLER and E. H. SWIFT *ibid.* **72**, 3767 (1950); N. H. NACHTRIEB and R. E. FRYXELL *ibid.* **71**, 4035 (1949); H. L. FRIEDMAN *ibid.* **74**, 5 (1952).
[27] H. M. N. H. IRVING, unpublished; V. I. KUZNETSOV *J. Gen. Chem.* U.S.S.R. **17**, 175 (1947).
[28] L. I. KATZIN, J. R. FERRARO, W. W. WENDLANDT, R. L. MCBETH *J. Amer. Chem. Soc.* **78**, 5139 (1956).

TABLE 3.—COMPOSITIONS OF ORGANIC LAYERS IN EQUILIBRIUM WITH SATURATED THORIUM NITRATE

Solvent comp. (%)[a]	Th (%)	$Th(NO_3)_4$ (%)	Water (%)	Water corr. (%)	Excess water (%)	H_2O/Th	Org./Th[b]
*iso*Butyl alcohol							
100	23·95	49·53	15·75	1·79	13·95	7·5	4·55
71·5	18·68	38·67	11·45	1·22	10·23	7·06	6·0
50·2	13·41	27·76	7·53	0·84	6·69	6·43	7·6
43·0	11·51	23·83	6·18	0·70	5·48	6·14	8·2
	10·70	22·13	5·95	0·72	5·23	6·30	9·1
33·3	8·22	17·02	4·66	0·55	4·11	6·44	10.0
	8·14	16·83	4·42	0·55	3·87	6·12	10·1
20·0	3·88	8·03	2·03	0·30	1·73	5·75	14·5
9·0	0·78	1·61	0·42	0·10	0·32	(5·3)	—
*iso*Butyl alcohol[c]							
100	23·6	48·8	15·2	2·06	13·1	7·15	
89·9	20·76	42·93	13·42	1·71	11·71	7·27	
77·7	18·40	38·05	11·00	1·37	9·63	6·74	
71·4	16·75	34·64	10·20	1·20	9·00	6·92	
63·8	phase separation						
Hexone							
100	22·68	46·90	12·15	0·30	11·85	6·74	4·2
	22·23	45·98	11·90	0·30	11·60	6·72	4·4
83·5	18·48	38·22	9·46	0·28	9·18	6·40	5·5
71·7	15·50	32·06	7·88	0·26	7·62	6·33	6·5
60·3	11·69	24·18	6·03	0·21	5·82	6·42	8·3
	11·35	23·48	5·66	0·21	5·45	6·18	8·7
43·2	4·26	8·81	2·24	0·18	2·06	6·23	21
33·5	1·12	2·32	1·27	0·12	1·15	13·2	67
25·2	0·21	0·43	0·53	—	—	—	—
20·1	0·00	0·00	0·36	—	—	—	—
Hexone[c]							
92·2	19·20	39·71	9·98	0·70	9·28	6·22	
85·5	17·71	36·63	9·12	0·60	8·52	6·20	
78	phase separation						
Diethyl ether							
100	21·08	43·59	12·38	—[d]	—	7·58	6·5
76·7	14·75	30·50	7·75	—	—	6·78	13
53·7	3·20	6·62	1·66	—	—	6·68	20
36·3	0·54	1·12	0·38	—	—	(4·4)	—
Ethylene glycol diethyl ether							
100	27·90	57·73	16·30	0·22	16·08	7·42	1·8
82·4	24·25	50·15	13·50	0·20	13·30	7·07	2·4
	phase separation						

TABLE 3—(*continued*)

Solvent comp. (%)[a]	Th (%)	$Th(NO_3)_4$ (%)	Water (%)	Water corr. (%)	Excess water (%)	H_2O/Th	Org./Th[b]
Ethylene glycol dibutyl ether							
100	14·24	29·46	5·75	0·20	5·55	5·02	6·1
84·1	8·86	18·33	3·69	0·19	3·50	5·09	9·9
77·8	6·83	14·13	2·81	0·16	2·65	5·00	12·6
61·2	2·50	5·17	1·22	0·14	1·08	5·5	31
42·7	0·70	1·45	0·40	0·12	0·28	5·1	—
Diethylene glycol diethyl ether							
100	27·80	57·49	16·12	0·19	15·93	7·38	1·36
85·2	25·37	52·47	14·15	0·19	13·96	7·09	1·61
		phase separation					
Diethylene glycol dibutyl ether							
100	21·65	44·79	8·90	0·35	8·55	5·09	2·3
68·9	15·45	31·97	6·42	0·10	6·32	5·28	2·9
43·9	8·07	16·70	3·18	0·05	3·13	5·00	4·6
26·9	0·96	1·99	0·47	0·01	0·46	6·2	29

[a] Per cent oxygenated component; second component, CCl_4.
[b] Oxygenated component/Th, corrected for CCl_4.
[c] *n*-Heptane diluent rather than CCl_4.
[d] Pure water solubility only 1·25%, so corrections less than for hexone (<0·20 at 100%).

active solvent with an inactive liquid. The conclusion is reached that with the common types of oxygenated solvents—alcohols, ketones, ethers—thorium nitrate is accompanied by 6–7 molecules of water. This, if the co-ordination number of thorium is 8, corresponds to perhaps two of the anions being held in the co-ordination sphere, and two held electrostatically. If the co-ordination number is greater than 8, then more of the anions are included in the co-ordination sphere. With solvents possessing butyl end groups, such as the dibutyl ethers of ethylene glycol and diethylene glycol, only five water molecules accompany each thorium nitrate, indicating that at least three anions are in the co-ordination sphere (Table 3).

With organic-substituted phosphoric acid derivatives, such as tributyl phosphate and dibutyl butylphosphonate, the organic phases obtained are essentially anhydrous, containing less than one molecule of water per thorium nitrate (Table 4). By molecular weight determinations in addition to the analytical data it is possible to show that the species in solution are of the type $Th(NO_3)_4 \cdot 2$tributyl phosphate and $Th(NO_3)_4 \cdot 3$tributyl phosphate. In the latter case, it is probable that the third organic group displaces one of the anions from the co-ordination sphere. Further, since tributyl phosphine oxide, containing a single oxygen, gives the same sort of species in benzene solution as does tributyl phosphate, it seems probable that each tributyl phosphate molecule is singly co-ordinated to thorium and that therefore the co-ordination number of the thorium in these solutions is but 6. Uranyl nitrate seems to behave in similar fashion with tributyl phosphate,[29,30] leading to an apparent

[29] L. I. KATZIN and R. L. MCBETH unpublished.
[30] T. V. HEALY and H. A. C. MCKAY *Trans. Faraday Soc.* **52**, 633 (1956).

TABLE 4.—COMPOSITIONS OF ORGANIC PHOSPHATE LAYERS IN EQUILIBRIUM WITH SATURATED THORIUM NITRATE

Solvent comp. (%)[a]	ThO_2 (%)	$Th(NO_3)_4$ (%)	H_2O (%)	H_2O/Th	P/Th
Tributyl phosphate					
100	22·92	41·67	0·58	0·37	2·50
84·6	20·88	37·96	0·49	0·34	2·47
59·2	16·24	29·53	0·45	0·40	2·53
38·4	11·90	21·64	0·38	0·47	2·50
20·8	6·83	12·41	0·15	0·32	2·64
6·60	2·18	3·96	0·04	0·3	2·89
Dibutyl butylphosphonate					
100	24·79	45·07	1·00	0·59	2·30
84·4	22·43	40·78	0·79	0·51	2·32
58·2	17·63	32·05	0·63	0·52	2·35
37·5	12·81	23·29	0·38	0·44	2·36
20·5	7·84	14·25	0·24	0·45	2·36
6·28	2·72	4·94	0·13	0·7	2·33
Tributyl phosphite[b]					
100	27·29	49·61	7·06	3·8	1·68
84·1	25·08	45·59	6·02	3·5	1·72
83·6	24·46	44·47	6·06	3·6	1·79
57·2	19·88	36·14	4·76	3·5	1·80
36·5	14·51	26·38	3·09	3·1	1·87
19·9	7·98	14·51	1·60	2·9	2·22
19·8	8·60	15·63	1·85	3·2	2·00
6·16	2·80	5·09	0·46	2·4	2·20

[a] Second component of solvent, CCl_4.
[b] H_2O/Th and P/Th taking water analyses at face value.

co-ordination number of 4, rather than the normal 6. It seems probable, therefore, that the type of co-ordination, electronically speaking, is different from the oxygen electron co-ordination of normal organic compounds, and that tributyl phosphate, like the halide ions, is capable of calling forth lower co-ordination numbers of its partner cations than they might normally show.

At this point it is appropriate to return to consideration of the salt type which was excluded in our first paragraph—the nonionic or definitely covalent salts. Examples of the type are the mercuric halides, stannic iodide, antimony tri-iodide, etc. In their water solutions they tend to be poorly ionized or un-ionized, and in addition to being soluble in the same organic solvents as the salts we have discussed most, they are soluble in chloroform, carbon tetrachloride, benzene, etc. Further characteristic of the covalent salts is relatively high volatility, and their general behaviour as uniary molecules, in contrast to the ionic salt types. One criterion for type of bonding is the effect on the magnetic properties of paramagnetic cations, and in many cases the ionic type of material, even when the cation is clearly involved in some sort of complex, gives magnetic indication of a continuing "ionic" character.

To this extent there is a physical basis for discrimination between the two types of salts.

Some points which blur this distinction will be emphasized, however. On the solubility side, $CoCl_2 \cdot 2H_2O$ is completely insoluble in liquids such as benzene, chloroform, or carbon tetrachloride. The corresponding pyridinate, however, has an appreciable though small solubility in these solvents. More provocative, perhaps, is spectral comparison of the effect of binding on the anions involved. If one compares the light absorption of cobaltous iodide and, for example, antimony tri-iodide, in alcohol solution, one finds the same absorption peaks for the iodide in the two instances,[31] drastically shifted from the absorption of the free ion. HgI_2, completely covalent, shows a shift which is much smaller than seen in the CoI_2 absorption. From the effects on the anion absorption, which is some sort of measure of the binding, one would say the Co(II) species in solution was as covalently bound as the others. More precise evaluation of the different criteria for binding, and better definition of what is meant must be achieved to characterize accurately the electronic differences between recognizable chemical behaviour differences.

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More can be said on the differences between the inorganic salts soluble in the oxygenated organic solvents, and those which are not. A group of the latter which may be dismissed in a few words are the salts of polyvalent anions. The lattice energies of these are so high that "driving force" sufficient to dissolve them in organic solvents does not present itself. In fact, a large fraction of such salts are insoluble, or of low solubility, in water itself. Further discussion will therefore be limited to salts of simple univalent anions, primarily nitrates and halides.

From what has been said above on the behaviour of the salts that do dissolve in the oxygenated solvents, it can be seen that two important factors are the strength with which anions and donor groups like water are held, and the lattice energy of the solids. For the salts of the alkali metals, for example, both factors are generally unfavourable. The tendency of these salts to crystallize in the anhydrous state is symptomatic of weak co-ordination of water, and at the same time gives the close ionic spacing which maximizes crystal lattice energies. For the smallest cation, lithium, the combination of greater water co-ordination ability seen in the occasional hydration of lithium salts, coupled with the weakening of lattice energies by considerable disparity in size with the anions, allows some solubility of lithium salts in alcohol and acetone. For the group as a whole, however, the strong binding of water characteristic of the transition elements is absent.

With the alkaline earths, hydrated solids are the rule. Even though the lattice energies of 2-1 salts are higher than those of the alkali halides, some nitrates and halides show considerable solubility in alcohols, sometimes in acetone, and occasionally even in ether. Organic solution tendency is higher for iodides and bromides than for chlorides, at least partially due to lower lattice energies (larger ionic radii). In general, the barium salts are less soluble than the magnesium and calcium salts, with weaker water binding by the larger barium cation more than offsetting the lattice-energy decrease of the large cation. The 3-1 rare-earth salts, with high lattice energy and relatively ready dehydration, generally show very low organic solvent solubility. For the 3-1 transition element salts, as has been said, the decisive factor seems to be the ability to take on co-ordination number 4. In the case of aluminium chloride,

[31] L. I. KATZIN *J. Chem. Phys.* **23**, 2055 (1955).

this ability is strong enough to give solubility of the salt even in benzene and other hydrocarbons, with the aid of the dimerization process. In the presence of moisture, however, the strong tendency to hydrolysis interferes. This points up the fact that salts which are soluble in organic solvents in the presence of water must strike a balance between sufficiently strong co-ordination to oxygen, and co-ordination so strong that the water molecule is disrupted.

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THE CONDUCTIMETRIC BEHAVIOUR IN NONAQUEOUS SOLVENTS OF ORGANOMETALLIC CHLORIDES FROM GROUP IVB

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Abstract—Conductance measurements have been made for solutions of organometallic chlorides and related compounds of the elements of Group IVB in pyridine, acetonitrile, nitrobenzene, pyridine-nitrobenzene mixtures, nitrobenzene-aluminium trichloride mixtures, and in liquid sulphur dioxide. It has been found that in general these solutes do not produce organometallic cations in solution, and especially that no resonance-stabilized cations are derived from triphenylchlorosilane or tris *p*-dimethylaminophenylchlorosilane in systems of Lewis acids. Furthermore, triphenylchlorosilane does not yield pyridinium ions with a triphenylsilyl substituent. Some evidence was found for ionization of organotin compounds, but it appears that ill-defined and special solvation conditions are necessary for this to occur.

SPORADIC interest in the electrolytic behaviour of organometallic halides of Group IVB has been reported in the literature during the last sixty years. Such interest has been reflected in work with organohalostannanes and organostannols in water,[1,2,3,4,5] in alcohols and aqueous solutions of alcohols,[2,3,6,7,8] and in solutions of nitrobenzene or acetone with pyridine or aqueous ethanol.[9] Also, some work has been reported for organolead compounds,[10,11] and with organochlorosilanes and silanols.[12,13,14,15]

This paper presents the results of research to ascertain whether or not cationic species containing elements of Group IVB were formed from typical organometallic solvents in the solvents studied. The results are limited to the detection of relatively large quantities of stable ions, as opposed to detection of very low concentrations of species which might form as unstable reaction intermediates. The method of electrolytic conductance was chosen as the most valid means of investigation for studying organometallic chlorides and related compounds in the nonaqueous solvents aceto-nitrile, pyridine, nitrobenzene, pyridine-nitrobenzene mixtures, nitrobenzene-aluminium tribromide mixtures, and liquid sulphur dioxide.[16] Special attention will

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[14] V. WANNAGAT and F. BRANDMAIR *Z. anorg. Chem.* **280**, 223 (1955).
[15] W. DILTHEY *Ber.* **36**, 923 (1903).
[16] For work using *N,N* dimethylformamide as a solvent and for notes on the purification of that solvent, see A. B. THOMAS and E. G. ROCHOW *J. Amer. Chem. Soc.* (in press).

be given to the behaviour of triphenylchlorosilane and organotin compounds in these solvents, for it serves to clarify earlier work reported in the literature.

EXPERIMENTAL

Apparatus and procedure

These have been described elsewhere.[16]

Materials. The preparation and purification of triphenylchloromethane, triphenylchlorosilane, triphenylchlorogermane, triphenylchlorostannane, trimethylchlorostannane, dimethyldichlorostannane, and triphenylchloroplumbane have been described elsewhere, as has the analytical procedure for determining chloride content.[16]

Tetrakis-*p*-dimethylaminophenylsilane was prepared by the method of GILMAN, PLUNKETT, and DUNN.[17] The compound was repeatedly recrystallized from benzene and from acetone, and the final material was free of chloride. M.p. 242°C (sealed tube).

Tris-*p*-dimethylaminophenylchlorosilane (crystal violet analogue for silicon) was prepared by the method of GILMAN, PLUNKETT, and DUNN,[17] as modified by WANNAGAT and BRANDMAIR.[14] The product was repeatedly recrystallized from dry benzene. M.p. 217°C (sealed tube); purity: 102 ± 0·5% of theoretical chloride content.

The addition compound dimethyldichlorostannane dipyridine was prepared by the method of KRAUS and GREER from pure dimethyldichlorostannane and conductance-grade pyridine.[18] M.p. 143°C (sublimed); purity: 99·4 ± 0·1% of theoretical chloride content.

Aluminium bromide was prepared by the method of JACOBER and KRAUS[19] and sealed into ampoules under vacuum.

Purification of solvents

Eastman spectro-grade acetonitrile was purified by the method of WAWZONEK and RUNNER.[20] Specific conductance at 25·00°C: 0·4–1·9 × 10^{-7} mho-cm^{-1}.

Merck reagent-grade pyridine was purified by distillation from aluminium trichloride at atmospheric pressure: it was then redistilled from solid potassium hydroxide at atmospheric pressure, and finally distilled from triphenylchlorosilane at atmospheric pressure. Specific conductance at 25·00°C: 1·1–3·0 × 10^{-8} mho-cm^{-1}. The proton-releasing impurity in this pyridine was found to be less than 10^{-4} M (expressed as water). (See ref. 16 for method of determination.)

Eastman Yellow Label nitrobenzene was purified by the method of BURGESS and KRAUS,[21] but, was fractionated only twice: once from aluminium trichloride and then from alumina. Specific conductance at 25·00°C: 1·4–2·8 × 10^{-9} mho-cm^{-1}.

Refrigeration grade "Extra Dry Es-O-Too" was dried in the gaseous state by slow passage through two 50 × 2·5 cm columns of Baker's C.P. anhydrous magnesium perchlorate and then condensed in a trap. This was followed by degassing for 1 hour at −78°C. All work with liquid sulphur dioxide was performed in a vacuum system and sulphur dioxide was distilled directly into dry conductance cells.* Specific conductance at 0°C: 0·866–1·88 × 10^{-7} mho-cm^{-1}.

RESULTS

Measurements are at 25·00 ± 0·01°C unless otherwise specified, and specific conductances, k, in mho-cm^{-1} given in the tables are corrected for the specific conductance of the solvent. Concentration of solute, c, is in mol/litre and molar conductance, Λ, is mho-cm^2/mol.

* The authors are indebted to Prof. N. N. LICHTIN and Dr. P. PAPPAS of Boston University, who performed all work with liquid sulphur dioxide.

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1. *Studies in acetonitrile*

TABLE 1.—TRIPHENYLCHLOROSILANE

$c \times 10^4$	$k \times 10^7$	Λ	Time (min)
1·795	1·52	0·847	1
	3·08	1·715	61
4·24	3·60	0·850	62
	4·20	0·991	92
12·0	4·83	0·403	93
	5·68	0·474	135
20·6	6·53	0·317	136
	12·93	0·627	856
22·6	13·83	0·612	857
	13·98	0·617	887

TABLE 2

Solute	$c \times 10^4$	$k \times 10^7$	Λ
Ph_3GeCl	7·99	0·52	0·0650
Ph_3SnCl	12·55	0·28	0·0233
Me_2SnCl_2*	17·8	2·22	0·125

* Temperature 33°C.

TABLE 3.—DIMETHYLDICHLOROSTANNANE DIPYRIDINE

$c \times 10^4$	$k \times 10^7$	Λ
0·886	9·17	10·35
2·11	19·57	9·28
3·22	29·5	9·17
4·04	37·6	9·33
5·00	49·1	9·82
5·72	56·6	9·90
6·96	69·9	10·03
7·98	84·9	10·6
9·55	105·9	11·08
11·18	124·1	11·12
13·35	150·4	11·25
15·19	170·9	11·25

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2. *Studies in pyridine*

TABLE 4.—TRIPHENYLCHLOROSILANE

$c \times 10^4$	$k \times 10^7$	Λ
4·96	24·0	4·84
8·98	32·4	3·60
14·70	41·1	2·80
27·2	55·2	2·03
35·2	56·3	—
39·6	56·5	—
44·5	56·6	—
69·0	57·1	—

Once constant conductance had been reached, only negligible changes with time occurred over 24-hour periods.

TABLE 5.—TRIPHENYLCHLOROMETHANE

$c \times 10^4$	$k \times 10^7$	Λ
12·73	7·6	0·596
30·3	13·6	0·449
56·9	24·5	0·431
94·0	38·9	0·414

The data in Table 5 apply to solutions of triphenylchloromethane made by adding triphenylchloromethane to a $3{\cdot}49 \times 10^{-3}$ M solution of triphenylchlorosilane in pyridine. This original solution was free of impurities that produce conductance, and the solvent correction, which has been applied to all the specific conductances in Table 5, was $k(Ph_3SiCl\ solution) = 24{\cdot}1 \times 10^{-7}$ mho-cm^{-1}.

TABLE 6.—TRIPHENYLCHLOROSTANNANE

$c \times 10^4$	$k \times 10^7$	Λ
4·81	1·415	0·2945
9·72	2·88	0·297
15·54	3·68	0·237

TABLE 7.—TRIMETHYLCHLOROSTANNANE

$c \times 10^4$	$k \times 10^7$	Λ
3·88	1·24	0·320
8·74	1·98	0·2265
12·48	2·57	0·206

TABLE 8.—DIMETHYLDICHLOROSTANNANE

$c \times 10^4$	$k \times 10^7$	Λ
3·61	1·41	0·390
9·05	2·35	0·260
18·35	3·51	0·191

Dimethyldichlorostannane was difficult to dissolve in pyridine, and a white coating formed on the crystals of solute, presumably the addition compound dimethyldichlorostannane dipyridine.

TABLE 9.—TRIPHENYLCHLOROPLUMBANE

$c \times 10^4$	$k \times 10^7$	Λ
0·997	0·144	0·1445
4·075	0·622	0·153
7·34	0·872	0·1186
12·05	1·58	0·1310
17·53	2·38	0·1355

Slight increases in conductances with time occurred for organotin and lead compounds in pyridine amounting to about 5% increase over several hours. The conductance of the most concentrated solution in Table 9 markedly decreased after about 12 hours.

TABLE 10

Solute	$c \times 10^4$	$k \times 10^7$	Λ
Ph_3CCl	11·1	0·155	0·140
Ph_3SiCl	3·8	0·263	0·069
$(p\text{-}Me_2NC_6H_4)_3SiCl$	11·1	0·496	0·0448
$(p\text{-}Me_2NC_6H_4)_4Si$	8·75	0·11	0·0126
Ph_3SnCl	10·35	0·10	0·00965
Me_2SnCl_2	17·8	0·58	0·0326

Tetrakis-*p*-dimethylaminophenylsilane is included here to show that it was essentially free of ionic impurities.

TABLE 11.—DIMETHYLDICHLOROSTANNANE DIPYRIDINE

$c \times 10^4$	$k \times 10^7$	Λ
2·98	1·54	0·517
6·12	3·92	0·641
9·60	7·08	0·738
14·85	12·19	0·821

Dimethyldichlorostannane dipyridine dissolved with difficulty in nitrobenzene.

3. *Studies in pyridine-nitrobenzene mixtures*

TABLE 12.—TRIPHENYLCHLOROSILANE ADDED TO PYRIDINE-NITROBENZENE

Total mols pyridine present: $3{\cdot}81 \times 10^{4}$; molarity of pyridine: $3{\cdot}74 \times 10^{-3}$ M.

Total mols Ph_3SiCl added $\times 10^{4}$	$k \times 10^{7}$	Elapsed time (min)
0·314	3·57	35
0·619	4·26	125
0·848	4·51	260
1·211	4·74	470
1·741	5·05	530
2·16	5·16	590
2·60	5·27	650

Estimated total mols of water: $1{\cdot}2 \times 10^{-6}$
Estimated molarity of water: $1{\cdot}2 \times 10^{-7}$ M.

TABLE 13.—TRIPHENYLCHLOROSTANNANE

Mols of pyridine: 0·01075: molarity of pyridine: 0·0131 M.

Total mols of Ph_3SnCl added $\times 10^{4}$	Ph_3SnCl $c \times 10^{4}$	$k \times 10^{7}$	Λ
0·844	1·025	2·04	1·99
3·214	39·1	6·79	0·173
3·706	45·0	7·67	0·170

4. *Studies in nitrobenzene-aluminium tribromide**

TABLE 14

Solute	Molarity of aluminium tribromide: $3{\cdot}34 \times 10^{-3}$ M		
	$c \times 10^{4}$	$k \times 10^{7}$	Λ
Ph_3SiCl	12·5	1·8	0·144
Ph_3CCl	5·7	107·2	18·85

The specific conductances of all solutions given in tables in this section have been corrected for the specific conductance of aluminium bromide solutions.

TABLE 15.—TRIS *p*-DIMETHYLAMINOPHENYLCHLOROSILANE

$c \times 10^{4}$	Molarity of aluminium tribromide: $3{\cdot}20 \times 10^{-3}$ M		
	$k \times 10^{7}$	Λ	Λ/*p*-$Me_2NC_6H_4$ group
11·95	380	31·6	10·5

TABLE 16.—TETRAKIS-*p*-DIMETHYLAMINOPHENYLSILANE

$c \times 10^4$	Molarity of aluminium tribromide: $6{\cdot}45 \times 10^{-3}$ M		
	$k \times 10^7$	Λ	Λ/*p*-$Me_2NC_6H_4$ group
7·93	467	59	14·75

5. Studies in liquid sulphur dioxide

TABLE 17.—TRIPHENYLCHLOROSILANE

$c \times 10^4$	$k \times 10^7$	Λ
15·5	2·26	0·146
16·6	2·43	0·146
	Temperature: 0°C	

DISCUSSION

1. Of the solutes measured in acetonitrile, only the addition compound dimethylchlorostannane dipyridine ionizes.

The conductances observed for triphenylchlorosilane are too low to be considered as evidence for true ionization of the solute. The observed conductances increase with time in spite of rigorous precautions to prevent access of moisture; it is concluded that traces of water in the purified acetonitrile were responsible for the conductances observed, and for the increase with time, since one hydrolytic product is hydrogen chloride. However, the possibility of some slight reaction between the solute and acetonitrile itself cannot totally be excluded.

The conductances given in this paper for triphenylchlorogermane, triphenylchlorostannane, and dimethyldichlorostannane can be explained in terms of hydrolysis of the solutes, none of which, however, hydrolyse nearly as readily or extensively as triphenylchlorosilane.

The conductances observed for dimethyldichlorostannane dipyridine cannot be explained in this manner; both their magnitude and constancy with time support the conclusion that the solute is ionizing in acetonitrile. A conventional plot of the data is shown in Fig. 1. The shape of the curve is not atypical of substances that ionize in a complex fashion to produce several species in solution; however, analysis of the present data is impossible. The conductance minimum and plateau support the contention that several species may be present, e.g. $Me_2SnPy_2Cl^+$, $Me_2SnPy_2^{++}$, $Me_2Sn(Py)^7Cl^+$, $Me_2SnPyCl_3^-$, Cl^- are possible (each solvated with acetonitrile)[7]. More accurate conductance data would be needed over a larger concentration range, as well as corollary experiments, to identify the ions and to specify the equilibria.

2. It can be seen in Table 4 that the specific conductances of solutions of

triphenylchlorosilane in pyridine become nearly constant at a concentration of about 3×10^{-3} M triphenylchlorosilane. Similar results were obtained for this compound with other samples of pyridine, and the conductance became constant at about 1×10^{-4} M triphenylchlorosilane. The conductance that is produced can be explained in terms of small amounts of proton-releasing impurities which may be present (e. g. water, primary and secondary amines)[7] and which are known to react rapidly and completely with organohalosilanes in basic media. It is apparent that quaternary ammonium ions with a triphenylsilyl substituent are not formed in measurable

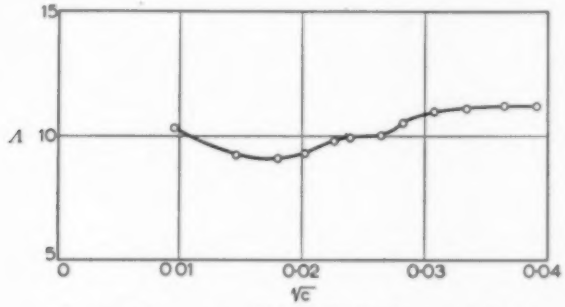

FIG. 1.—Phoreogram of $Me_2SnCl_2 \cdot 2Py$ in acetonitrile

concentration, since the solutions of triphenylchlorosilane at higher concentration do not change in conductance even upon standing overnight.

The behaviour of triphenylchloromethane is in marked contrast, since conductance increases with concentration of the solute, as would be expected if triphenylmethylpyridinium ions are forming in solution. These increases cannot be ascribed to impurities, since triphenylchloromethane was added to a pyridine-triphenylchlorosilane solution that had reached constant conductance, instead of to a fresh batch of pure pyridine.

The low magnitude of specific and molar conductances for triphenylchlorostannane, trimethylchlorostannane, dimethyldichlorostannane, and triphenylchloroplumbane force the conclusion that these solutes do not form ions in pyridine, and the conductances observed are produced from slight solvolysis with impurities. The decrease in specific conductance with time noticed for triphenylchloroplumbane can possibly be explained by the formation of complex anions of triphenylchloroplumbane, e.g. Ph_3PbCl^{9-}, which form by capture of chloride ions by triphenylchloroplumbane. This reaction would occur to a very slight extent, as would the solvolysis responsible for the presence of chloride ion.

3. None of the solutes measured in nitrobenzene gave evidence of electrolytic behaviour to any sensible degree, except possibly the addition compound dimethyldichlorostannane dipyridine. The molar conductance for this latter compound increased with increasing concentration—a phenomenon difficult to explain. It may be that the recorded values do not represent equilibrium values, or that several competing reactions are occurring either between the solute and solvent or between the solute and impurities in the solvent, and that these reactions are producing small amounts of ionic products which combine with molecules in solution to give secondary

ionic products that are more conducting than the original ones; such complex equilibria could conceivably lead to higher molar conductances at higher concentrations.

The values of specific conductance for dimethyldichlorostannane dipyridine are not large, but if desired, a rough value for an ionization constant can be assigned by assuming that the compound is behaving as a 1-1 electrolyte and by arbitrarily designating the molar conductance at infinite dilution as equal to 25 (a typical value for electrolytes in nitrobenzene). Classically, such considerations yield an ionization constant of 1×10^{-7} for dimethyldichlorostannane dipyridine, using data for the most dilute solution in Table 2.

4. The addition of triphenylchlorosilane to a dilute solution of pyridine in nitrobenzene produced only very small amounts of conductance, as shown in Table 12. The conductances increased with time and became essentially constant after the time-intervals indicated. Since it has been demonstrated that the pyridine used contained minute amounts of water, it must be concluded that the consumption of this water and the subsequent production of pyridinium chloride was responsible for the conductance. Reverse experiments performed by adding pyridine to a solution of triphenylchlorosilane in nitrobenzene corroborate this viewpoint, since an increase in conductance was observed which was roughly proportional to the amount of pyridine added, even though the amount of pyridine present was in excess of the equivalents of triphenylchlorosilane.

The low conductances observed for triphenylchlorostannane in a mixture of pyridine and nitrobenzene render it doubtful that the solute ionizes in this medium; but an ionization constant of $1{\cdot}5 \times 10^{-8}$ can be assigned if desired, again assuming the molar conductance at infinite dilution to be 25, and using data for the most concentrated solution in Table 13.

5. Table 14 clearly contrasts the behaviour of triphenylchlorosilane and triphenylchloromethane in the powerful acidic system of aluminium tribromide and nitrobenzene. The known ionization of triphenylchloromethane is demonstrated and the absence of such behaviour for the analogous silicon compound is obvious. In this system no resonance-stabilized siliconium ions are produced. Solutions of aluminium tribromide did not change colour when triphenylchlorosilane was added, whereas the solutions of triphenylchloromethane became a deeper red-brown.

The crystal violet analogue for silicon is compared with the tetrakis-*p*-dimethylaminophenylsilane in Tables 15 and 16. The silicon analogue might be expected to be one of the most likely compounds of silicon to yield resonance-stabilized siliconium ions in the presence of Lewis acids, but identical behaviour for the tetrakis compound rules out the detection of this. The conductance per *p*-dimethylaminophenyl group is approximately constant. (Were conditions of concentration of solute and aluminium tribromide more nearly the same, closer agreement would be expected.) Both of these compounds react in the same way toward silver perchlorate in nitrobenzene or in benzene, producing a deep red colour in solution (or a precipitate in benzene). This colour change was observed for both compounds with the aluminium tribromide solutions. Similar colour changes may be obtained with the parent amine, *p*-dimethylaminobromobenzene. It must be concluded that the colour changes and conductances arise from an attack by acidic reagents on the nitrogen of the *p*-dimethylamino groups rather than from the formation of siliconium ions.

The data in Table 17 show that no siliconium ions are produced in liquid sulphur dioxide: comparable conductances would have been obtained with triphenylchloromethane at only $1{\cdot}1 \times 10^{-6}$ M. The triphenylchlorosilane solutions were colourless.

General conclusions. Pyridinium ions with triphenylsilyl substituents did not form in the systems investigated here, and it may be that the absence of such quaternization is general for the elements of Group IVB, other than carbon. Certainly organohalosilanes differ from organic halides in their reactions with amines, viz. the reluctance of organohalosilanes to form addition compounds even with amines, the absence of salt-like properties for those addition compounds which are known, and the disparity of behaviour between analogous systems of organic halides and organohalosilanes which with the former compounds readily produce quaternary ammonium salts. The present work demonstrates also that with representative compounds of the remaining elements of Group IVB there is little evidence for the formation of quaternary ammonium ions from pyridine. While it is certain that the ability of the elements of Group IVB to form addition compounds with amines increases as one goes down the group, it is very doubtful that true quaternary salts are formed. A formal explanation to supplement this argument can be given by considering that if an amine be added to a halide of carbon and a new compound is to result which has real chemical bonds (as opposed to a mixture of the two materials with perhaps van der Waals forces acting), then the new compound must be ionic, since no orbitals are available in either carbon or nitrogen which would allow a covalency greater than 4. With other elements of the group, however, higher covalencies become increasingly more favourable with respect to energy as one goes down the group, and thus stable addition compounds having *covalent* bonding are possible as well as compounds having ionic bonding. The chemical evidence favours covalent bonds as being the rule rather than the exception in these cases, and bears out the contention that "quaternary nitrogen ionic-bonds" do not form with silicon, germanium, tin, or lead. It is not inconceivable, however, that proper choice of an *anion* could promote the the establishment of such a bond with these latter elements.

The nonexistence of resonance-stabilized triphenylsiliconium ions and the lack of evidence for a similar ion from tris-*p*-dimethylaminophenylchlorosilane in systems which produce large amounts of analogous carbonium ions support findings reported earlier.[12,14] The present work lends credence to the contention that silicon does not form double bonds with carbon of the π type. The nonexistence of coloured compounds of silicon is noteworthy in this connection.

The inogenic behaviour of organotin compounds in the present nonaqueous solvents is not clearly established, although ionogenic behaviour in water has clearly been shown elsewhere.[5] In the present work the addition compound dimethyldichlorostannane dipyridine gave evidence of complex electrolytic behaviour in acetonitrile, and this same compound (as well as triphenylchlorostannane) in a pyridine-nitrobenzene mixture gave slight evidence for electrolytic behaviour. Other situations did not give evidence for ionization of organotin compounds (see also ref. 16). There is no doubt that under other and more appropriate conditions of solvation, organotin halides are capable of ionization. In aqueous solution, for instance, cationic species containing tin are obtained from dimethyldichlorostannane. This was expected from cryoscopic measurements[5] and confirmed by a conductance experiment: an $8{\cdot}10 \times 10^{-3}$ M solution of dimethyldichlorostannane in conductance

water gave a specific conductance of $2{\cdot}29 \times 10^{-3}$ mho-cm^{-1} at 25·00°C and had a pH of 2·78. Subtraction of the specific conductance due to the concentration of hydrogen present leaves a residual conductance of $1{\cdot}59 \times 10^{-3}$ mho-cm^{-1} which can only arise if cationic species of tin are present. A similar experiment shows that tin-containing cations arise from trimethylchlorostannane in water.

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THE CHEMISTRY OF THORIUM—VIII*

SOME ELECTROCHEMICAL CHARACTERISTICS OF ANHYDROUS THORIUM CHLORIDE IN ANHYDROUS ETHYLENEDIAMINE

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Abstract—Anhydrous thorium chloride dissolves vigorously and readily in anhydrous ethylenediamine. The resulting solutions show the conductance behaviour of solutions of weak electrolytes. Electrolysis of such solutions gives cathodic evolution of hydrogen and transport of thorium to the anode compartment, but does not give cathodic deposition of thorium metal.

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THE highly electropositive nature of thorium precludes its electrodeposition from aqueous solutions of its salts.[1] Although it is perhaps logical to assume that conditions more favourable to electrodeposition might exist in nonaqueous systems, available published data are essentially negative. Thus, no thorium deposits have been obtained from liquid ammonia,[2, 3] pyridine,[4] or alcoholic[4, 5] solutions of thorium salts, although mixed thorium and zinc deposits have been described for electrolysis of ethanolic solutions of thorium and zinc chlorides containing reducing agents such as formaldehyde or hydroxylamine hydrochloride.[4] Cathodic deposits consisting of organo-thorium combinations have been described in some instances.[4]

It is reasonable to believe that successful deposition of the metal is most likely under strictly anhydrous conditions with solvents which are sufficiently basic in character to favour stabilization of strongly reducing states. The desirable electrolytic characteristics of anhydrous ethylenediamine[6] and the success which has been achieved in the electrodeposition of certain rare-earth metals from this medium[7–10] suggested investigation of the behaviours of ethylenediamine solutions of anhydrous thorium salts. Summarized in this communication are solubility, conductance, and electrolysis data for solutions of the anhydrous chloride. This salt was selected because it combines excellent solubility characteristics with inherent ionic character and the absence of any reducible species other than the thorium ion.

* For Part VII see T. MOELLER and M. TECOTZKY. *Anal. Chem.* **27**, 1056 (1955).

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[8] T. MOELLER and P. A. ZIMMERMAN *Science* **120**, 539 (1954).
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[10] G. W. CULLEN Doctoral dissertation, University of Illinois (1956).

EXPERIMENTAL

Materials employed. Commercial ethylenediamine, containing *c.* 15% water, was dehydrated and purified as previously outlined.[11] The product had a specific conductance of $1{\cdot}11 \times 10^{-6}$ mho cm^{-1} at 25°C. It was stored under dry nitrogen in glass-stoppered flasks. These were kept in desiccators containing soda lime, magnesium perchlorate, and phosphorus(V) oxide and were opened only in a dry-box.

Chemically pure thorium chloride was dissolved in hydrochloric acid and freed of traces of iron(III) by double extraction with ethyl ether. Crystalline thorium chloride 8-hydrate was then obtained by shaking with an equal volume of ethyl ether and saturating with dry hydrogen chloride gas at 0°C. After being dried over magnesium perchlorate, the product contained small quantities of hydrogen chloride. *Anal.* Calcd. for $ThCl_4 \cdot 8H_2O$: Th, 44·8; found: Th, 45·7.

Anhydrous thorium chloride was obtained from the 8-hydrate by HECHT's thionyl chloride procedure[12] in essentially the same fashion as described by BRADLEY, SAAD, and WARDLAW.[13] The product dissolved readily and completely in water by a highly exothermic process. It contained no more than traces of thionyl chloride and hydrogen chloride. *Anal.* Calcd. for $ThCl_4$: Th, 62·05; found: Th, 62·13.

Manipulation. All anhydrous materials were handled under carbon-dioxide-free dry nitrogen in a "Gloved Box, Berkeley Type," Model R1104, supplied by Radioisotope Applications Company, Albany, California. Solutions prepared in this box were transferred to glass-stoppered containers which could be sealed with "Biseal" self-bonding tape before removal to the atmosphere.

Solubility determinations. Anhydrous thorium chloride was added slowly, and with vigorous shaking, to 60 ml of anhydrous ethylenediamine until a sizable amount remained undissolved. Portions of the resulting suspension were transferred to centrifuge tubes fitted with ground-glass stoppers. The sealed tubes were removed from the dry-box and thermostated at $30 \pm 0{\cdot}05$°C for a week, during which period they were often shaken vigorously. The tubes were centrifuged for 15 min and opened in the dry-box. Aliquots of the clear supernatant liquids were analysed for thorium by precipitating the hydrous oxide with excess water and weighing as the ignited oxide.

Conductance measurements. Conductance values were obtained at $25 \pm 0{\cdot}05$·°C at definite dilutions as previously outlined,[11] using a Leeds and Northrup Conductivity Bridge, Model 4866, and a cell with bright platinum electrodes. The cell constant was 2·013 cm^{-1}.

Electrolysis experiments. Electrolysis was carried out in a 60-ml cell of the type described by MOELLER and ZIMMERMAN.[11] In a typical experiment, a solution containing 57·41 g of anhydrous thorium chloride per litre was electrolysed with 1·5 cm × 2·9 cm bright platinum electrodes placed 5 cm apart and separated by a medium-porosity sintered-glass disk. Current was supplied from a 300-V d.c. source at an initial cathode density of 5 mA/cm^2 and a potential drop of 70 V. Gases liberated were allowed to escape through "Tygon" tubes, the ends of which were immersed in paraffin-oil.

RESULTS AND DISCUSSION

Solubility in anhydrous ethylenediamine. The solubility of anhydrous thorium chloride in anhydrous ethylenediamine at 30°C is 110·8 g/litre, or 0·296 mole/litre. This is a value considerably in excess of the solubilities found for anhydrous rare-earth metal salts.[7, 9–11] Its magnitude may be the result of extensive solvation of the solute. This is suggested by the highly exothermic character of the dissolution process. Recovery of the solvated solute by evaporation of the solutions to viscous syrups was not effected. There is no evidence of extensive solvolysis of the salt, but the solvent undergoes some decomposition as a result of heat liberated on dissolution and becomes yellowish.

Conductance studies. Conductance data, as summarized in Table 1 and in Fig. 1, indicate that thorium chloride behaves as a weak electrolyte in anhydrous ethylenediamine. This is analogous to the behaviour of anhydrous salts of the tripositive

[11] T. MOELLER and P. A. ZIMMERMAN *J. Amer. Chem. Soc.* **75**, 3940 (1953).
[12] H. HECHT *Z. anorg. Chem.* **254**, 37 (1947).
[13] D. C. BRADLEY, M. A. SAAD, and W. WARDLAW *J. Chem. Soc.* 2002 (1954).

rare-earth metal ions[7, 9–11] and of a number of other salts[14] and is consistent with what might be expected for a compound containing a highly-charged ion dissolved in a solvent of only moderately large dielectric constant (16 at 25°C).

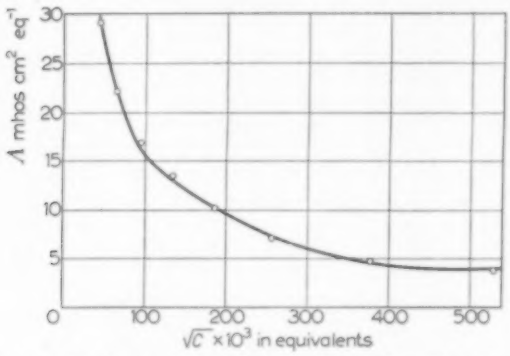

FIG. 1.—Conductance of ethylenediamine solutions of thorium chloride.

TABLE 1.—CONDUCTANCE DATA FOR ETHYLENEDIAMINE SOLUTIONS OF THORIUM CHLORIDE AT 25°C

Concentration c equiv/litre	$\sqrt{c} \times 10^3$	Equivalent conductance mho cm² equiv⁻¹
0·2793	529	4·26
0·1397	374	5·32
0·0699	264	6·48
0·0350	187	10·35
0·0175	132	13·20
0·0088	94	16·82
0·0044	66	22·05
0·0022	47	29·30

Electrodeposition studies. During electrolysis, the cathode-current density and the potential drop across the cell increased over a period of some 7 hours. Considerable hydrogen was evolved at the cathode, and fine, needle-shaped white crystals, insoluble in ethyl ether but giving a test for chloride ion in aqueous solution, separated in the anode compartment. There was no visible or otherwise detectable deposit on the cathode. The anode solution became hot and assumed a reddish-brown colour, probably because of oxidation by liberated chlorine. Analyses of the catholyte and anolyte solutions after electrolysis showed a depletion of thorium content in the cathode compartment which was almost exactly balanced by a gain in thorium in the anode compartment.

Under the conditions employed, no electrodeposition of thorium was effected. This cannot be ascribed to any lack of ionic character in the solution used, since the conductance is reasonably large. However, transport of thorium to the anolyte

during electrolysis suggests the presence of anionic thorium-containing species which may not reduce readily to the metal. Under comparable conditions, ethylenediamine solutions of rare-earth metal salts undergo complete stripping of rare-earth metal ion in the cathode compartment and depletion of rare-earth metal ion in the anode compartment.[9, 10]

Although electrodeposition of the metal was not effected, the solutions studied are sufficiently interesting from the electrochemical point of view to merit further study.

Acknowledgements—Grateful appreciation is expressed for support received by the junior author from Smith-Mundt and Fulbright Awards.

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THE REMOVAL OF PLUTONIUM BEFORE THE ANALYSIS OF MIXED FISSION PRODUCTS

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Abstract—Methods are presented for the complete removal of up to 100 mg of plutonium as an initial step in the radiochemical analysis of certain individual products in irradiated plutonium metal or plutonium-uranium alloy.

TECHNOLOGICAL research on methods of using plutonium as a nuclear fuel often requires analyses for individual fission products, e.g. to trace their path in possible chemical processes of purifying used fuel. Satisfactory methods are in general available[1] for the radiochemical separation of radioactive isotopes of these elements, including a comprehensive scheme which has already been tested on 20-mg samples of irradiated uranium and plutonium,[2] but these methods do not provide for the removal of plutonium at the start of the analytical manipulations. This element presents rather elaborate requirements for safe chemical manipulation. We attempted completely to remove the plutonium, without significant loss of carrier-free fission products. (The steps necessary to secure complete interchange between radioactive isotope and stable carrier, e.g. an alkaline fusion would have presented manipulative difficulties which we have sought to avoid.) The absorption of the nitrate complex of Pu(IV) on to an anion exchange resin[3] is reported to be very specific for this element and has been used to purify it from uranium and fission products. We have established conditions for the complete removal of up to 100 mg plutonium from nitric acid solutions, using the anion resin De-acidite-FF. Of the nongaseous elements listed above, all except zirconium and niobium were recovered in 98% or greater yield on washing the resin. An auxiliary method is presented to deal with these two elements.

EXPERIMENTAL

1. *Retention of plutonium(IV) by De-acidite-FF*

Solutions of about 10 mg/ml of plutonium(III) chloride in dilute HCl were oxidized by adding solid $NaNO_2$ and making 7 N in HNO_3. The solution was freed from alpha-active Am^{241}, daughter of Pu^{241}, by anion exchange, as described in the method. The alpha activity remaining in solution was due to Pu^{239} and Pu^{240} and was used for tracer measurements.

De-acidite-FF was purchased from Messrs. Permutit Ltd. as the air-dried chloride form, of 8% nominal cross linking, particle size −16 to +50 mesh, and was ground in a coffee-mill and sieved to −60 to +100 mesh. It was stirred with 7 N HNO_3 immediately before use and slurried into a vertical tube, 6-mm internal diameter, the resin being held in place by a constriction and a plug of glass-wool. About 0·8 g of air-dried resin (chloride form) is sufficient to form a column with a volume of 2 ml

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(3) W. M. CAMPBELL *Nucleonics* **92** (1956).

and of vertical height about 6 cm. The column was washed with 200 ml of nitric acid of the appropriate strength, usually 7 N, before use. Distribution measurements were made by shaking portions of pretreated resin with tracer solutions of plutonium(IV) in nitric acid. The rate of reaching equilibrium increased as the particle size decreased, e.g. tests with De-acidite-FF gave the results shown in Table 1.

The distribution coefficent K_D is defined as the weight of plutonium taken up per gram of 110°C oven-dried resin, divided by the weight of plutonium per millilitre of aqueous phase after shaking.

TABLE 1.—RATE OF UPTAKE OF Pu BY DE-ACIDITE FROM 7 N HNO_3

Particle size	Time of shaking				
	5 min	15 min	30 min	1 hr	3 days
	values of apparent K_D				
50 microns	4700	4700	3700	4700	—
−60 to +100-mesh	560	1400	1900	2500	6600
−16 to +50-mesh	230	450	700	1100	5400

The 60–100-mesh resin was convenient to prepare and use.

Using this grade of resin, and shaking for 3 days, we obtained K_D values of >4000 from solutions of plutonium(IV) in 3 N, 7 N and 11 N HNO_3. Because the absorption of the plutonium was so strong, no attempt was made to determine the optimum acidity within the range studied.

The capacity of the standard column of resin for plutonium was measured by passing through the column a solution of Pu(IV) in 7 N HNO_3, containing about 3 mg Pu/ml, at a flow rate of 0·2 ml/min, until significant alpha activity was detected in the solution leaving the column. This "breakthrough point" was reached when the dark-green band due to absorbed plutonium could be seen by eye to reach the bottom of the column. Using one particular batch of resin, 0·1% breakthrough of the added plutonium was observed for a column load of 216 mg: this represents about 80% of the saturation capacity of this batch of resin for this element.

A second batch of resin gave a lower breakthrough capacity, which still exceeded 100 mg per column.

In the fission product separation described below, loads of up to 100 mg Pu per standard column were frequently applied at flow rates of up to 0·2 ml/min and plutonium was never detected (<0·1%) in the fission product fraction.

The plutonium is probably held on the resin as an anionic complex of the type $Pu(NO_3)_6^{2-}$. It resists washing with up to 100 column volumes of 7 N HNO_3 at 2 ml/min (<0·1% detected in washings), but this is partially or completely removed by acids which form strong neutral or cationic complexes, e.g. HF, H_2SO_4, H_2O_2, $H_2C_2O_4$. The results shown in Table 4 illustrates this point. The plutonium may be stripped quantitatively from the resin by reduction of the Pu(IV) complex, e.g. with hydroxylamine. The column is first washed with 2 ml of N HNO_3 and then with 8 ml of a 5% solution of $NH_2OH{\cdot}HCl$.

It is advisable to store the De-acidite-FF resin in the chloride form: the resin first darkens and then slowly bleaches if allowed to stand for several days in the presence of 7 N HNO_3 and we have found some indications that the bleaching is accompanied by a loss in capacity.

2. *Quantitative recovery of fission products*

Distribution coefficients were measured for various individual fission products (obtained from the Radiochemical Centre, Amersham), in 3 N, 7 N, and 11 N nitric acid. The mixture was shaken for 3 days. The results are shown in Table 2.

The results for zirconium and niobium were influenced by the concentration of oxalic acid.

Column experiments were made to test the recovery of fission products on washing the resin with up to 200 ml of 7 N HNO_3. The fission products were obtained as separated fractions from R.C.C.

TABLE 2.—DISTRIBUTION COEFFICIENTS FOR DE-ACIDITE-FF

Conc. of HNO_3	3 N	7 N	11 N
Fission product			
Cs^{137}	—	0	—
Sr^{90}	0	0	0
Ce^{144}	1	4	3
Ru^{106} (as nitroso trinitrate)	20	12	8
$Zr^{95} + Nb^{95}$ (in 0·00003 M oxalic acid)	23	24	36
Zr^{95} (in 0·003 M oxalic acid)	0	2	17
Nb^{95} (in 0·003 M oxalic acid)	1	2	30

or were prepared as a mixture by pile irradiation of small quantities of plutonium. The recoveries were tested in one or more of three ways, (a) gamma-counting of aliquots taken from solutions of individual fission products before and after passing through the column, (b) gamma-counting the washed resin after treating a solution of mixed fission products; in many cases this was extended to make an approximate analysis by gamma scintillation spectrometry, (c) radiochemical analysis for individual fission products retained on the resin, after treating a solution of mixed fission products. The results for each element are summarized in Table 3.

TABLE 3.—RECOVERIES OF INDIVIDUAL FISSION PRODUCTS FROM DE-ACIDITE-FF

Fission product	Volume of washings (ml)	Method of testing recovery	% recovery
Sr^{90}	200	(c)	99·5
$Zr^{95} + Nb^{95}$	200	(b)	86, 88, 91
Mo^{99}	200	(c)	98·7
Ru^{103}	200	(b)	98·7, 98·5, 98·4
Ru^{106}	60	(a)	100·0, 99·8
Te^{132}	200	(b)	99
I^{131}	200	(b)	98·8, 96·8, 96·7
Cs^{137}	200	(c)	99·2
Ce^{141}	200	(b)	99·6 99·8
Ce^{144}	20	(a)	100·0, 100·0

Attempts were made to improve the recoveries of Zr^{95} and Nb^{95} by washing with 7 N HNO_3 containing various complexing anions (Table 4), but in each case this led to excessive loss of plutonium, which was added at tracer levels.

The results show that the present method of removing plutonium permits a quantitative recovery of all the elements tested except zirconium and niobium, which suffer variable losses of up to 20%. These elements are best determined in a separate aliquot of the plutonium solution. The plutonium is reduced to Pu(III) and is then precipitated with lanthanum as the trifluoride. The supernatant solution is further scavenged with another addition of lanthanum, leaving less than 0·1% of the plutonium in solution. It is necessary to add zirconium carrier to the original aliquot, and subsequently to determine the chemical yield—for some zirconium is lost by co-precipitation with plutonium and lanthanum. The addition of HF to the solution and prolonged stirring of the precipitate brings about exchange between Zr^{95} and inactive zirconium: this exchange would not have been complete in the 7 N HNO_3 solution used in the previous method. The chemical yield of zirconium carrier after removing the plutonium in the manner indicated above was 67%. Niobium carrier was also added to the original aliquot, and was recovered in 100% yield.

TABLE 4.—REMOVAL OF Zr, Nb, AND Pu ON WASHING DE-ACIDITE-FF

Added anion	% recovery of Zr + Nb	% leakage of Pu
0·001 M fluoride	98·2	29
0·01 M fluoride	99·2	30
0·1 M fluoride	100	57
0·001 M oxalate	96·7	4·6
0·01 M oxalate	97·3	2·3
0·05 M oxalate	97·5	38
0·0005 M sulphate	92·5	1·1
0·002 M sulphate	95	0·5
0·25 M sulphate	97·9	1·2
2·5 M sulphate	98·8	8·3
0·25 M sulphate plus 1·0 M H_2O_2	97	6

RECOMMENDED PROCEDURE FOR REMOVAL OF PLUTONIUM FROM STRONTIUM, YTTRIUM, MOLYBDENUM, RUTHENIUM, TELLURIUM, IODINE, CAESIUM, BARIUM, CERIUM, LANTHANUM, AND OTHER RARE EARTHS

The initial dissolving and chemical treatment of the plutonium must be carried out in an enclosed glove-box; the ion-exchange step may be handled in a fume cupboard in a class 1 radiochemical laboratory[4] and subsequent steps in a class 1 or 2 laboratory.

Samples of irradiated plutonium metal or plutonium-uranium alloy are dissolved in moderately concentrated HCl or HCl-HNO_3 respectively. An appropriate aliquot is diluted to an acidity of 1·0 N, and solid $NH_2OH{\cdot}HCl$ is added (ten times the weight of plutonium present), and dissolved. The mixture is allowed to stand for 1 hour, to complete the reduction of all the plutonium to Pu(III). The plutonium is now oxidized to Pu(IV) by adding solid $NaNO_2$ (twenty-five times the weight of plutonium present) and stirring. The mixture is made 7 N in HNO_3 and is allowed to stand for 1 hour to complete the evolution of the gaseous products of the oxidation.

The solution of Pu(IV) in 7 N HNO_3 is passed at 0·2 ml/min through 2 ml of pretreated resin as described above, and is collected below the column, together with the washings (see below). The column, prepared properly, will hold at least 100 mg plutonium and this will be seen as a dark-green band—the exact capacity for 99·9% retention, is best determined experimentally for each new batch of resin. The quantity of plutonium added should always be less than that required to extend the dark-green band to within 1 cm of the bottom of the column.

The column is washed with 200 ml of 7 N HNO_3 at 2 ml/min. The combined solutions will now contain less than 0·1% of the original plutonium, but will contain part of any neptunium and all of any americium or higher actinide present in the sample. These elements include long-lived alpha emitters, which are just as toxic as plutonium. The alpha activity due to these elements will depend on the source and

[4] H. J. DUNSTER *Medicine Illustrated* **8**, 11 (1954).

history of the plutonium: in our analyses it did not exceed 1% of the alpha activity due to the plutonium.

The nitric acid solution is analysed for radioactive fission products by conventional methods.[1] The anion exchange resin may be extruded or slurried out into a polythene cell, which is then sealed and examined for small amounts of residual fission products, using a gamma spectrometer.

RESULTS

A mixed solution of tracer plutonium and fission products, prepared from irradiated plutonium, was analysed as above, and also by conventional methods without removing the plutonium—which was not an embarrassment in this special instance. The results for Sr^{89}, Ca^{137}, Ba^{140}, Ce^{141}, and La^{130} given in Table 5 are satisfactory.

TABLE 5.—RECOVERIES OF SOME COMMON FISSION PRODUCTS

Fission product	Method A	Direct analyses	% recovery
	Corrected counts min^{-1} per aliquot		
Sr^{89}	1,830	1,940	94
Cs^{137}	1,800	1,800	100
Ba^{140}	1,200	1,260	95
Ce^{141}	18,900	19,400	97·5
La^{140}	32,700	33,200	98·5

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THE ADDITION PRODUCTS OF HEAVY-ION BOMBARDMENT OF TANTALUM

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Abstract—An investigation has been made of the products obtained by bombarding tantalum with ions of C^{13}, C^{13}, and N^{14}. Mercury, gold, and platinum activities in the 187-, 188-, and 189-mass chains were looked for. Evidence is presented that a previously observed 4·5-min activity in gold may be assigned to Au^{188}. An accurate value for the half-life of Hg^{189}, viz. 23 ± 2 min, was obtained by a milking experiment.

THE light mass chains of mercury, gold, and platinum have been studied by SMITH and HOLLANDER,[1] both by fast-proton bombardment of gold and by carbon ion (C^{12}) bombardment of tantalum. We have tried to extend this work by bombarding tantalum also with C^{13} and N^{14} ions, using the six-charged internal beams in the Nuffield cyclotron of the University of Birmingham. For the approach of such ions to a tantalum nucleus the potential barrier is close to 60 MeV, which is also the most probable energy in the beam spectrum. Tantalum, in addition to its favourable mechanical properties, makes a good target by virtue of its consisting of essentially only one isotope. This fact facilitates discussion of the mass assignment of product nuclei.

After bombardment, chemical separations of mercury, gold, platinum, and sometimes also iridium were made. Care was taken that these were decontaminated from possible fission products, in particular tellurium, since this element has some chemical similarities to mercury and gold. In some bombardments activities associated with tellurium were observed, but systematic work on fission products is not yet complete.

EXPERIMENTAL

(a) *Bombardments*. Targets of tantalum foil 40 μ thick were bombarded for periods ranging from a few minutes to some hours, on an internal probe at a standard radius, following our usual technique.[2] Beam currents measured after traversal of the target were usually of the order 10^{-8} A. After the end of the bombardment the target was removed and chemical operations begun, in general within 1 min.

(b) *Chemistry*. The targets were invariably dissolved in a minimum of 27 N HF and 16 N HNO_3 with the addition of 100–1000 μg quantities of carriers for mercury, gold, platinum, tellurium, and, if necessary, iridium. These elements were then recovered by precipitation with stannous chloride. Thereafter the procedure varied, depending on which isotopes were being investigated. The unseparated mixture, without further chemical treatment, was counted under a G.M. counter, and gave a gross decay curve whose principal components were of about 40-min and 10-hr half-life, followed by a long component of several days, the counting rate being too low to permit of an accurate determination.

Distillation of the mixture under vacuum yielded a sublimate of mercury and tellurium, giving essentially the same gross decay curve.

Mercury and tellurium were separated from each other by repeated precipitation of the former with sodium hydroxide in the early experiments, but a much more satisfactory method was evolved using an Amberlite (I.R. 400) anion exchange column. In this procedure, the metallic precipitate

(1) W. G. SMITH and J. M. HOLLANDER *Phys. Rev.* **98**, 1258 (1955).
(2) K. F. CHACKETT, J. H. FREMLIN, and D. WALKER *Phil. Mag.* **45**, 173 (1954).

was redissolved in aqua regia and the gold removed by extraction into amyl acetate. The aqueous phase was evaporated and brought to a low HCl content. It was then passed down a column of Amberlite (250-mesh) 13–15 mm long, 0·055 cm² cross-section. With 0·1 N HCl as eluant at a flow speed of 0·1 to 0·2 ml/min, the recovery of tellurium was complete in 2 min or less. The mercury was then eluted with 2 N HNO_3. This elution seemed to depend on the complete displacement of chloride ion from the column, and therefore depended on whether the HCl content of the initial solution had been reduced satisfactorily. Control experiments showed that the mercury fraction so obtained would be completely free from gold, even if any of this element were present in the solution put on the column. Decontamination from platinum is, however, not good; about one-third of the platinum initially present would be eluted with the mercury. Final decontamination from platinum may be achieved by vacuum distillation of the mercury, but we found this was never necessary because we could easily distinguish between the mercury and platinum isotopes on the basis of half-life.

Since mercury isotopes may be produced by nitrogen-ion bombardment of tantalum, but not by carbon-ion bombardment, we were able to check the efficacy of the mercury separation by treatment of nitrogen- and of carbon-bombarded targets by identical procedures. In this way we could be sure that activities found in mercury in nitrogen bombardments were correctly ascribed to mercury. It is noteworthy that we found small activities in tellurium both with nitrogen and carbon-ion bombardments.

The filial relationship between the gold and mercury isotopes was examined by the well-known milking technique, gold being extracted by amyl acetate from a pure mercury fraction in 6 N HCl solution. This experiment was carried out some six times, the successive gold extractions being made at intervals of 10, 15, or 20 min. A correction was made to allow for the not negligible extraction of parent mercury into the organic layer. By this means a single mercury activity was found, with half-period 23 ± 2 min. Owing to the time taken in the separation of the mercury initially we should not have detected a parent mercury of half-life much shorter than 5 min. There was no evidence of a longer activity, or at least of one giving a gold daughter detectable by our G.M. counters. The value given above for the half-life is the mean of the six results, all of which lay within the limits quoted.

(c) *Counting*. Mercury and gold samples were counted under standard end-window Geiger counters; magnetic analysis showed that the radiations detected were largely electrons (i.e. conversion electrons from γ transitions following electron-capture processes), rather than positrons. The only case wherein positrons were definitely observed was after rapid chemical separation of gold was carried out, when a 4·5-min component was present. This activity has previously been reported by THOMPSON *et al.*[2] the mass being left uncertain at 185–188.

In none of the samples did we find alpha emission above the background (0·3 c.p.m.) of a zinc sulphide screen scintillation counter. The alpha/electron-capture ratio for all the isotopes studied is therefore in general well below 1/1000.

The decay of mercury samples was investigated, using activated sodium iodide crystals for X and γ rays and an anthracene crystal for electrons, with a photomultiplier tube and a single or multichannel analyser. However, in no case could we find a radiation which decayed with a half-life corresponding with that obtained in the milking experiment (23 min), periods of about 42 min, i.e. that of the daughter Au^{189}, always being observed. This reflects the evident complexity of the decay schemes involved. When a 1-mm-thick sodium iodide crystal was used, the X-ray peak also showed the 42-min decay, and this is indeed what would be expected, since the *K* X rays of gold and platinum would not be resolvable; the composite decay curve of a 23-min parent and 42-min daughter counted with the same detection efficiency would appear as an almost perfect exponential with a 42-min period. This is because the half-life ratio is so close to 1 : 2.

RESULTS

Bombardments with C^{12}, C^{13}, and N^{14} all gave strong 42-min decays in the gold fractions, with which were associated the 11-hr daughter activity as expected for Pt^{189}. The following Ir^{189} activity was also observed, although at the low level of

[2] S. G. THOMPSON *et al.* *Phys. Rev.* **76**, 1426 (1949); J. O. RASMUSSEN JR., S. G. THOMPSON, and A. GHIORSO *Phys. Rev.* **89**, 33 (1953).

intensities we could achieve we could not measure the half-life accurately (accepted value, 11 days). As has already been stated, the 42-min gold appears as a daughter of 23-min mercury in the nitrogen bombardments.

In addition, all these bombarding ions gave a 4·5-min activity in gold: this was strongest for C^{12} and weakest for N^{14}. No daughter activity could be definitely associated with this.

Finally, we observed a 15-min activity in gold after C^{13} bombardments and more strongly after C^{12} bombardments. This was associated also with a 2·5-hr activity, presumably the daughter Pt^{187}. The expected 12-hr Ir^{187} daughter was also found in separations of platinum, and of iridium after bombardments of some hours' duration with C^{13}.

All these results are consistent with the production of members of three decay chains. Their relative yields cannot be estimated accurately from our counting data because overall counting efficiencies are not known. However, the trends can be shown quite clearly as regards the effect of the three bombarding ions. This has been done in Table 1, where the numbers refer to "countable" atoms, i.e. counting-rate times half-life, for the three gold activities, normalized to $Au^{189} = 1$. In this table the figure for the 42-min chain takes into account the existence of the Hg^{189} parent.

TABLE 1.—RELATIVE YIELD OF GOLD ISOTOPES FROM HEAVY-ION BOMBARDMENTS OF TANTALUM

Bombarding ion	Half-life of Au member of chain		
	4·5 min	15 min	42 min
C^{12}	10	2·5	1·0
C^{13}	0·4	0·6	1·0
N^{14}	0·15	not detected <0·01	1·0
Mass assignment	188	187	189

DISCUSSION

As has been shown by BURCHAM and HAYWOOD,[4] the bombardment of platinum with nitrogen ions and of gold with C^{13} ions gives addition products in which seven or fewer neutrons are lost from the compound nucleus: the most probable product is that for which five neutrons have been lost. In the case of tantalum as the target element, one would not expect the situation to be very different, so that for C^{12}, C^{13}, and N^{14} bombardments the maximum yields should be in the 188-, 189-, and 190-mass chains respectively.

On the basis of the yield figures for C^{12} bombardments given in Table 1, we therefore suggest that the 4·5-min activity should be assigned to mass-188, its yield being four times that in the mass-187 chain and ten times that in the mass-189 chain. It is true that these large ratios might be partly due to greater counting efficiency for the conversion electrons, positrons, and γ rays of the 4·5-min activity, than for the

[4] W. E. BURCHAM and B. C. HAYWOOD *Proc. Phys. Soc.* A69 862 (1956).

conversion electrons and γ rays from the other gold isotopes. The positrons would certainly be counted more efficiently than some of the conversion electrons. However, magnetic analysis showed that the ratio of positrons to conversion electrons was not large. It does not seem likely, therefore, that the relative counting efficiencies could account entirely for such large ratios in the yield figures. Moreover, if the 4·5-min activity were really Au^{186}, the yield would be much less than that of Au^{187}, because this would represent the loss of seven neutrons from the compound nucleus.

For the C^{13} bombardments the yield figures are so much more nearly equal that no definite conclusions on this matter can be drawn. For the N^{14} bombardments the figures again point strongly to the mass-188 assignment for the 4·5-min activity; the yield is at least fifteen times too high for the mass to be 186. Indeed, for the formation of Au^{187} by N^{14} bombardment no less than eight neutrons must have been lost from the compound nucleus, which is hardly possible on energetic grounds, and it would hardly be surprising if the yield of Au^{186} were smaller still by two or three orders of magnitude.

We have not obtained any evidence for the production of members of the mass-190 chain, which should in fact be formed in good yield in the nitrogen bombardments. It would appear that their half-lives are either short (less than about 1 min) or rather long (10 days or more).

The only evidence which appears to contradict the mass-188 assignment we suggest is the observation by THOMPSON *et al.* of α activity associated with the 4·5-min period. The assignment to mass-188 might be taken to imply a still shorter period for Au^{187} instead of the observed period of 15 min. However, the ratio of α emission to electron capture in the 4·5-min isotope is small (less than 1 in 10^4). Our observations on Au^{187} do not preclude this ratio from being larger than this, although still less than 1 in 10^3. Consequently, the observed half-lives are still almost entirely controlled by the probability of electron capture. While it is usual to find a steady decrease in half-life as one proceeds to lighter isotopes of any element in this region, there are of course several other cases where an isotope has a longer-lived neighaour of smaller mass.

The mercury parents of the shorter-lived gold isotopes are themselves too short-lived to be measured by our techniques, but, as has been stated, we have derived a figure of 23 ± 2 min for the half-life of Hg^{189}. While this is in agreement with previously obtained values, it should be pointed out that the electron and γ spectra are complex and we have been unable to detect any radiation decaying with this period which we could resolve from the Au^{189} decay. This appears to cast some doubt on the observation by GILLON *et al.*[5] of electrons supposedly from conversion of γ rays of 28·6 KeV, from a source obtained by distilling what was believed to be mercury from a gold target bombarded with protons of >65 MeV. In our present work, in which we have made a compound nucleus of roughly the same excitation energy, we have observed tellurium activities, which would also have distilled under the conditions used by GILLON *et al.* We suggest therefore that the 28·6-KeV γ ray reported was in fact the *K* X ray of iodine and the electrons observed were photo-electrons from the gold plate on to which the source had been distilled. The tellurium isotope involved would be the well-known Te^{131} (half-life, 25 min).

[5] L. P. GILLON, K. GOPALAKRISHNAN, A. DE-SHALIT, and J. W. MIHELICH *Phys. Rev.* **93**, 124 (1954).

It is of interest with heavy-ion bombardments to find evidence of whether complete fusion of projectile and target nucleus occurs. Thus in the case of Au^{189} formed in N^{14} bombardments of tantalum, this isotope may be derived partly by neutron emission from a mercury compound nucleus to Hg^{189}, followed by electron capture, and partly by emission of neutrons and one proton from a mercury compound nucleus. We tested these possibilities by determining the Au^{189} yield during a short uniform bombardment, and comparing this with the Au^{189} yield from subsequent decay of the Hg^{189} atoms formed in the same bombardment. The results showed that the rate of production of Au^{189} by all other processes is less than 5% of that descending from Hg^{189}.

There is a strong inference that the lighter mass chains also start almost wholly from the mercury isotopes. This follows not only by analogy, but also from the more specific consideration that the immediate precursor of these chains is more likely to be an excited state in Hg^{189} emitting further neutrons, than an excited state in Au^{189} emitting neutrons. The presence of excited Au^{189} atoms, indicating the occasional emission of a proton as well as neutrons from the compound nucleus, could hardly fail to be betrayed by the presence also of an independent yield of ground state Au^{189}. If, indeed, the mass-188 chain starts at Hg^{188}, it follows that the half-life of this isotope is much less than 23 min, and probably much less than 5 min; otherwise, Au^{188} would have been detected in the second, and possibly later, separation of gold in the milking experiments.

Acknowledgements—We should like to thank the cyclotron team for making the bombardments, and Miss G. HAINE for invaluable assistance in the counting and computation of results. The work was facilitated by a contract with A.E.R.E., Harwell.

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LETTERS TO THE EDITORS

Oxidation and thermal decomposition of sodium and potassium borohydrides*

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RELATIVELY little has been reported on the air oxidation or the decomposition of the alkali metal borohydrides, MBH_4. SCHLESINGER and BROWN[1] state that lithium borohydride does not react with dry air at ordinary temperatures. When heated in a vacuum, lithium borohydride melts between 275° and 280° with the slow evolution of hydrogen and the formation of $LiBH_2$. Others[2] have found lithium borohydride to decompose above 200° by prolonged heating in vacuum. Sodium borohydride has been heated to 300° in air without apparent change.[3] When heated in vacuum, it is reported to be stable to 400°, but above 400° a slow evolution of hydrogen occurs.[3] Above 550° the decomposition of sodium borohydride becomes rapid, hydrogen and traces of diborane being evolved.[4] Potassium borohydride has been reported [5] to begin to decompose in a vacuum at about 500°, liberating hydrogen and potassium.

It is well known that sodium and potassium borohydrides are readily ignited and burn smoothly in air,[6] but no specific reaction with oxygen has been reported.[7]

We have studied the behaviour of sodium and potassium borohydrides heated in air, nitrogen, and hydrogen, using a recording thermobalance[8] in conjunction with apparatus for differential thermal analysis.† The heating rate was 9° per minute. Sodium borohydride of better than 98% purity was obtained from Metal Hydrides Inc. and used without further purification. Potassium borohydride was prepared by the method of BANUS, BRAGDON, and HINCKLEY,[5] and found to contain 70·57% K and 19·53% B, ratio K/B, 3·62 (theory for KBH_4: K, 72·47%; B, 20·05%; ratio K/B, 3·62). The borohydrides, oxidation products, and thermal decomposition products were titrated with acid to the methyl red endpoint to determine the base, and the boron was determined by titration with base after the addition of mannitol.[9]

Our results, summarized in Table 1, agree with the general observation that potassium borohydride is more stable and less reactive than sodium borohydride. In air, both compounds are converted quantitatively at elevated temperatures to the corresponding meta-borates, no further changes occurring below the meta-borate melting-points. There was no evidence of the formation of stable intermediates, such as "hypoborates," during the oxidation process. In both hydrogen and nitrogen, sodium and potassium borohydrides appear stable to relatively high temperatures, and then decompose in a complex manner involving the incomplete volatilization of both the alkali metal and the boron, the latter probably as hydride. Decomposition in hydrogen begins at a somewhat higher temperature than in nitrogen, suggesting that part of the initial decomposition may involve the reversible evolution of hydrogen. Differential thermal analysis data obtained simultaneously disclosed no significant changes other than those accompanying the weight changes.

Sodium borohydride heated in air gained weight. The nonvolatile product was analysed for sodium and boron, with three different experiments giving the results: Na, 34·5, 34·8, 35·2; B, 16·3, 16·7, 16·5 wt.%; theoretical for $NaBO_2$: Na, 35·0; B, 16·5.

* Taken from the Ph.D. thesis of ANTON G. OSTROFF.

† We are indebted to Professor LEROY EYRING for assistance and advice in the construction and operation of apparatus used in this work.

(1) H. I. SCHLESINGER and H. C. BROWN *J. Amer. Chem. Soc.* **62**, 2429 (1940).
(2) Metal Hydrides Inc. Technical Bulletin 402-B—Lithium Borohydride.
(3) H. I. SCHLESINGER, H. C. BROWN, H. R. HOEKSTRA, and L. R. RAPP *J. Amer. Chem. Soc.* **75**, 199 (1953).
(4) Metal Hydrides Inc. Technical Bulletin 502-D—Sodium Borohydride.
(5) M. D. BANUS, R. W. BRAGDON, and A. A. HINCKLEY *J. Amer. Chem. Soc.* **76**, 3848 (1954).
(6) N. G. GAYLORD *Reduction with Complex Metal Hydrides* pp. 17, 19. Interscience, New York (1956).
(7) *Ibid.* p. 40.
(8) F. A. MAUER *Rev. Sci. Instrum.* **25**, 598 (1954).
(9) H. C. BROWN, H. I. SCHLESINGER, I. SHEFT, and D. M. RITTER *J. Amer. Chem. Soc.* **75**, 192 (1953).

TABLE 1.—SUMMARY OF RESULTS

Compound	Atmosphere	Initial wt. change (°C)	Approx. temp. of complete reaction (°C)	Max. temp. (°C)	Nonvolatile products
$NaBH_4$	air	294	420	447	$NaBO_2$
$NaBH_4$	nitrogen	503	—	598	(Na,B)*
$NaBH_4$	hydrogen	512	620	637	(Na,B)*
KBH_4	air	356	480	1003	KBO_2
KBH_4	nitrogen	584	—	737	(K,B)*
KBH_4	hydrogen	626	660	741	(K,B)*

* Black, partly water insoluble solids, varying in composition, apparently containing both metal and boron, and evolving gas on contact with water.

Potassium borohydride heated in air also gained weight. The nonvolatile product was analysed for potassium and boron, three different experiments giving the following results: K, 47·7, 47·6, 49·0; B, 13·1, 13·1, 13,6 wt. %; theoretical for KBO_2: K, 47·7, B, 13·2. The differential thermal analysis curve showed an endothermic peak at 941°, presumably indicating the melting of the KBO_2.

When the sodium borohydride was heated in an atmosphere of hydrogen or nitrogen, it showed initially a small, unexplained weight loss followed by a gain to nearly its original weight, before major decomposition began. No similar behaviour was noted for potassium borohydride. Products of these decompositions were not identified; evidently hydrogen, some alkali metal, and some boron (presumably as a hydride) were lost by volatilization.

Calculations according to the "principle of electronegativity equalization"[10] indicate both $NaBH_4$ and KBH_4 to be completely ionic. It is suggested that the difference between the two may be related to differences in polarization of the BH_4^- anion by the cation, the lesser effect being exerted by the larger cation, of potassium. This implies that distortion of the anion decreases thermal stability and enhances chemical reactivity. Other experimental evidence consistent with this implication will be reported soon.

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[10] R. T. SANDERSON *J. Chem. Educ.* **32**, 140 (1955).

Proton magnetic resonance absorption in ferrocene and dibenzenechromium*

(*Received* 3 *December*, 1956)

WE have undertaken a study of line widths of proton magnetic resonance absorption at different temperatures in sandwich compounds with a view to elucidating their molecular structure and with special reference to any motion of the organic rings in these compounds. This note presents preliminary observations on ferrocene and on dibenzenechromium; the latter has been obtained by one of us (E. O. F.)[1] recently, using a system:

$$CrCl_3 + AlCl_3 + Al + C_6H_6$$

The line widths (distance between maximum and minimum peaks of the first derivative of the absorption curve) were measured with a variable-frequency nuclear-magnetic spectrometer.[2]

* Supported by Office of Naval Research, under Contract No. NONR-1866 (13). Reproduction in whole or in part is permitted for any purpose of the U.S. Government.
[1] E. O. FISCHER and W. HAFNER *Z. anorg. Chem.* **286**, 146 (1956).
[2] R. V. POUND and W. D. KNIGHT *Rev. Sci. Instrum.* **21**, 219 (1950).

A new cryostat[2] with a built-in R.F. coil was used. This arrangement prevented condensation of moisture on the sample tube at low temperatures and permitted changing of samples without disturbing the position of the sample in the uniform part of the magnetic field. A mechanical stage[3] was used for locating and clamping the sample in this position.

Ferrocene gives a line width of 4·0 gauss at 25°, at 0°, and at −23°. This decreases to about 2·2 gauss around −79° and broadens again to 4·2 gauss at −196°. The narrow line at room temperature is quite liquid-like, and supports the concept of rotation of the cyclopentadiene rings in ferrocene. Theoretical and experimental evidence for this rotation has been reviewed by PAUSON.[4] The unexpected narrowing of the line around −79° may be due to (second-order) phase transitions. This is being re-examined critically to obtain a plausible explanation of the apparent narrowing.

Dibenzenechromium gives a line width of about 3·0 gauss at 25°, at 0°, and at −23°. It shows a slight increase to 3·2 gauss at −79°. At −196° it gives an exceedingly broad, quite solid-like line 12 gauss wide. The narrow line at room temperature is again taken as evidence of the motion of the benzene rings, which motion appears to be frozen out at −196°; any probable transition is expected to lie between −79° and −196°.

The close-packed cubic lattice ($a = 9{\cdot}67 \pm 0{\cdot}03$ Å) of dibenzenechromium[5] seems to account for the ease with which the motion of the benzene ring is "frozen out" and indicates that it has a more rigid structure than ferrocene, which crystallizes in the monoclinic system.[6,7,8]

Further work on the dependence of line widths at other temperatures is in progress and is designed to elucidate the nature of the motion of benzene rings in dibenzenechromium.

A duplicate set of measurements was made on another sample of dibenzenechromium, kindly furnished by Dr. H. H. ZEISS of Monsanto Chemical Co., Dayton, Ohio, and prepared by an entirely new method.[9] Measurements at room temperature were also checked against a "Numar" spectrometer of the Nuclear Magnetic Corporation, Boston. We wish to thank Dr. WESTBAUM for providing these facilities.

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[2] L. N. MULAY To be published.
[4] P. L. PAUSON *Quart. Rev.* **9**, 400 (1955).
[5] E. WEISS and E. O. FISCHER *Z. Anorg. Chem.* **286**, 142 (1956).
[6] P. F. EILAND and R. PEPINSKY *J. Amer. Chem. Soc.* **74**, 4971 (1951).
[7] J. D. DUNITZ and L. E. ORGEL *Nature* **171**, 121 (1953).
[8] W. PFAB and E. O. FISCHER *Z. Anorg. Chem.* **274**, 316 (1953).
[9] H. H. ZEISS and W. HERWIG *J. Amer. Chem. Soc.* **78**, 5959 (1956).

ANNOUNCEMENT

In order to simplify the publishing mechanics and speed up the rate of publication of individual papers, the *Journal of Inorganic and Nuclear Chemistry* will, after the completion of the present volume, be published in volumes containing four issues each, and issues will follow each other at approximately six-week intervals. The publishing date will not be rigidly fixed, since it is the policy of the publishers to publish an issue as soon as it is ready so that the publishing delay may be cut down to a minimum, in the interests of contributors. Each volume, of course, will continue to contain approximately 400 pages, but will now be contained in four issues instead of in six.

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THE BETA SPECTRUM OF CARRIER-FREE Ni^{63}*

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Abstract—A method is given for the preparation of appreciable quantities of practically carrier-free Ni^{63} from pile irradiations of copper via the $Cu^{63}(n,p)$ reaction, which has an effective cross-section of 3 millibarns for the neutron spectrum encountered in a typical LITR irradiation. The beta spectrum was studied in a large gas proportional counter with carrier-free Ni^{63} mounted on a saturation thickness of platinum foil placed as a platform inside the sensitive volume. The allowed Fermi-Kurie plot appears to be linear to 7·5 keV, which suggests that the decay probably belongs to the class of allowed transitions with exceptionally long half-lives, interpreted to be "*l*-forbidden." The endpoint of the beta-spectrum occurs at 67·0 ± 0·5 keV.

The irradiation of spectroscopically-pure copper oxide powder produced appreciable amounts of Co^{60} and Zn^{65} corresponding to 0·6 p.p.m. cobalt and 1–2 p.p.m. zinc as subspectroscopic impurities in the target material.

THE decay scheme, disintegration energy, and half-life of Ni^{63} are reasonably well established. However, the comparative half-life is somewhat large for an allowed transition ($\log ft = 6{\cdot}73$ for $T_{\frac{1}{2}} = 125$ years[1]). It would appear that this transition is a member of a class of allowed transitions with exceptionally long half-lives, interpreted by NORDHEIM[2] as "*l*-forbidden"; that is, involving a change of two units of orbital angular momentum. These *l*-forbidden transitions exhibit allowed spectral shapes. There seems to be no agreement, however, regarding the shape of the beta spectrum of Ni^{63} ($E_{max} = 67$ keV) except perhaps that it is *not* of the allowed shape. Fermi-Kurie plots have exhibited deviations from linearity below 30 keV,[3–6] suggesting a first-forbidden decay. The principal experimental difficulty in the accurate determination of the shape of the spectrum has been the unavailability of sources of sufficiently high specific activity. The development of a technique for the preparation of carrier-free Ni^{63} seemed of importance for the re-examination of the spectrum, particularly at very low energies.

Since the $Cu^{63}(n,p)$ reaction is exoergic by 720 keV because of the n–H mass difference, a thermal neutron pile irradiation will produce an appreciable yield. At the same time, microgram quantities of stable Ni^{64} from the $Cu^{63}(n,\gamma)Cu^{64}(\beta^+,EC)Ni^{64}$ process and stable Zn^{64} from Cu^{64} beta decay are expected to be formed. Other

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‡ These authors found $\Delta J = 2$, yes shape. Such an α-shape is in disagreement with *ft* value and shell-model predictions (cf. WAY, KING, MCGINNIS, and VAN LIESHOUT *Nuclear Level Schemes*, $A = 40$ to 92, U.S. Office of Technical Services Report TID-5300 (1955)).

§ These investigators found the FK-plot concave toward the energy axis below 30 keV, with Oak Ridge Ni^{63} stock of comparatively low specific activity.

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[5] Y. KOBAYASHI, G. MIYAMOTO, and S. MORI *J. phys. Soc. Japan* **8**, 684 (1953).‡
[6] J. P. MIZE and D. J. ZAFFARANO *Phys. Rev.* **91**, 210A (1953); U.S. Atomic Energy Commission Report *ISC*-347 (1953).§

(n,p) reactions in this region have been shown to proceed with high yields.[7] The problem was thus one of making a carrier-free separation of nickel from gram quantities of irradiated copper. To accomplish this we have modified the method of HERBER and IRVINE[8] and MOORE and KRAUS[9] who showed that Ni(II) exhibits negligible absorption on Dowex-1 anion exchange resin, whereas Cu(II) has a maximum retention in 7 N HCl.[10] To eliminate solids from the resin, it was found essential to pass about 10 column-volumes of 12 N HCl through the column before use.

To check the method, a 0·25 g sample of copper was dissolved in aqua regia, evaporated to 1 ml, with frequent additions of HCl along the way to expel all traces of (deleterious) nitric acid, and tracer Ni^{63} (activity 2×10^{10} c/m per gram) was added. The solution, which was 12 N in HCl, was added to a Dowex-1 $\times$ 8 resin column (100 $\times$ 25 mm) in the form of quaternary ammonium chloride, and eluted with less than half a column volume of 7 N HCl. This effects an exceptionally clean separation of tracer Ni^{63} with 90–95% yield from macro amounts of copper; furthermore, the specific activity of the tracer (Oak Ridge Ni-63-P, Processed, High Specific Activity, batch No. 10) was approximately doubled, indicating the presence of non-nickel solids in the ORNL stock.

A 2 g sample of "Specpure" CuO powder, containing less than 5 p.p.m. cobalt and less than 10 p.p.m. zinc as subspectroscopic impurities,[11] was irradiated in the Oak Ridge LITR at a flux of about $8{\cdot}6 \times 10^{12}$ neutrons/cm^2-sec for 21 days. The sample was allowed to age for several weeks to permit 12·8 hour Cu^{64} to decay. It then was examined in a NaI(Tl) scintillation spectrometer before chemical separation, and appreciable amounts of Co^{60} and Zn^{65} activities were identified. Quantitative studies showed that the Co^{60} yield (3×10^{12} atoms/gram copper target) corresponded to about 0·6 p.p.m. cobalt impurity; thus, nothing can be said of the possibility of a $Cu^{63}(n,\alpha)Co^{60}$ reaction, which would be exoergic by about 1·5 MeV.[12] The yield of Zn^{65} corresponded to 1–2 p.p.m. zinc impurity.

After separating Ni^{63} carrier-free according to the above procedure, which, in one cycle, also removes Co^{60} and Zn^{65} activities, the nickel fraction was evaporated to dryness and weighed. The sample essentially was weightless and practically invisible. The absolute yield in this irradiation was measured by 4π counting and found to be $4{\cdot}4 \times 10^{14}$ atoms of Ni^{63} per gram copper, assuming a 125-year half-life;[1] this corresponds to an effective cross-section of $3{\cdot}1 \pm 0{\cdot}5$ mb for the neutron spectrum encountered by the sample in the LITR. This agrees with an estimate of 3·5 mb from the nomogram of INTHOF.[13]

The beta-spectrum was studied in a large gas proportional counter similar to that described in detail by MIZE and ZAFFARANO,[6] and which was filled to 1 atm with a 10% methane–90% argon mixture. Carrier-free Ni^{63} was mounted on a platinum platform (0·125 mm thick) placed internally some 4 cm from the centre wire and held at a positive potential appropriate to its position in the radial electrical field. Pulses were amplified by a Higinbotham non-overloading linear amplifier, selected by a

[7] B. L. ROBINSON and R. W. FINK *Bull. Amer. phys. Soc.* II **1**, 40, JA7, and erratum (1956).
[8] R. H. HERBER and J. W. IRVINE JR. *J. Amer. chem. Soc.* **78**, 905 (1956).
[9] G. E. MOORE and K. A. KRAUS *J. Amer. chem. Soc.* **74**, 843 (1952).
[10] B. G. HARVEY Elution Position Curves for Dowex-1. Private communication (1955).
[11] Johnson, Matthey, and Co., Ltd., Laboratory Report No. 8455 (1956).
[12] Computed from tables given by A. H. WAPSTRA *Physica* **21**, 385 (1955).
[13] W. INTHOFF *Nucleonics* **13**, No. 11, 67 (1955)

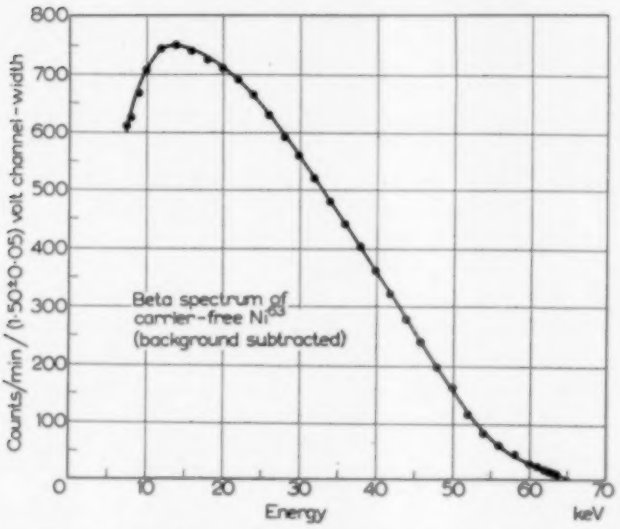

FIG. 1a.—Beta spectrum of carrier-free Ni^{63} mounted on a saturation backscattering thickness of platinum, uncorrected for finite instrument resolution, but with background spectrum (~69 c.p.m./channel between 25 and 75 keV) and the Fe^{55} peak (5·9 keV) subtracted. This curve is representative of data taken in several additional runs.

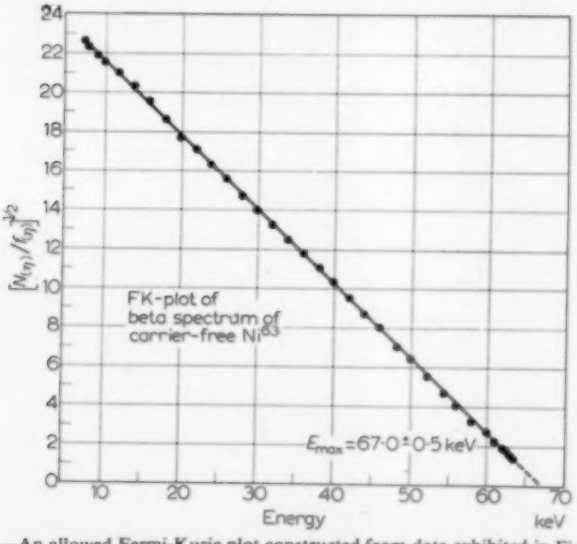

FIG. 1b.—An allowed Fermi-Kurie plot constructed from data exhibited in Fig. 1a. Linearity is observed from the 67·0 keV endpoint down to 7·5 keV, assuming tentatively that the saturation backscattering from platinum backing is energy-independent below 90 keV (see text). The effect on the spectrum of the finite resolution correction according to the method of OWEN and PRIMAKOFF (*Phys. Rev.* **74**, 1406 (1948)) was examined, as well as the effect of the change in resolution with energy (40% at 5·9 keV, 28% at 10·5 keV, etc., to 8·5% at 60 keV). These corrections had essentially no effect on the endpoint and only slight effect on the spectral shape, not exceeding the statistical precision of counting. The data shown above have not been corrected for resolution, because the magnitude of the correction was less than the uncertainty which remains from possible distortion owing to the superposition of a saturation backscattering spectrum upon the true spectrum. These studies are being extended in an effort to elucidate the effect of backscattering below 67 keV on the spectral shape (see text).

single-channel analyser, and counted manually on a scaler. Energy calibration was accomplished with carrier-free Fe^{55} as an internal standard (5·9 keV) which was placed on the wall of the counter, the linearity having been established up to 60 keV with the following external radioactive sources: Se^{75} (10·5 keV), Cd^{109} (22·1 keV), Sn^{113} (24·1 keV), and Os^{185} (60 keV). The background spectrum was taken carefully before and after the Ni^{63} spectrum, and subtracted. The data are shown in Fig. 1a from which the allowed FK-plot shown in Fig. 1b was constructed.[14] The FK-plot is linear to 7·5 keV (see caption) and exhibits an endpoint of $67{\cdot}0 \pm 0{\cdot}5$ keV. Because of the presence of the Fe^{55} standard on the walls of the counter, the spectrum was not investigated below 7·5 keV. SCHONLAND[15] demonstrated that backscattering of monoenergetic electrons from saturation thicknesses of gold is substantially independent of energy between 10 and 90 keV, although at higher energies there is an energy dependence.[16] However, the study of the Ni^{63} beta spectrum is being continued to examine the question of distortion due to backscattering.

The present result suggests that the beta transition is not first-forbidden. In summarizing beta transitions, MAYER and JENSEN[17] suggest an $f_{5/2}$–$p_{3/2}$ shell-transition assignment for Ni^{63} decay, which thus would be *l*-forbidden. A high-resolution magnetic-beta-spectrometer study of carrier-free sources is now feasible and should be undertaken to examine this question further.

In addition to the beta-spectrum analysis, other experiments with carrier-free Ni^{63} suggest themselves. For instance, about 10^{15} atoms would suffice for an experimental determination of the nuclear spin and magnetic moment by the hyperfine structure of the microwave paramagnetic resonance,[18] or by the method of atomic beams.[19]

[14] Using *Tables for the Analysis of Beta Spectra* (U.S. Dept. of Commerce, National Bureau of Standards, Applied Mathematics Series No. 13, June, 1952).
[15] B. F. J. SCHONLAND *Proc. roy. Soc.* **A108**, 187 (1925).
[16] S. C. CURRAN, in *Beta- and Gamma-ray Spectroscopy* (Ed. K. Siegbahn) Chap. VI. Interscience Publishers, Inc., New York (1955).
[17] M. G. MAYER and J. H. D. JENSEN *Elementary Theory of Nuclear Shell Structure* John Wiley, New York (1955).
[18] C. D. JEFFRIES Private communication (March, 1956).
[19] N. F. RAMSAY *Molecular Beams* Oxford University Press, New York (1956).

J. Inorg. Nucl. Chem., 1957, Vol. 4, pp. 237 to 238. Pergamon Press Ltd., London

PRODUCTION OF CARRIER-FREE Mg^{28} FROM ALUMINIUM*

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Abstract—Carrier-free Mg^{28} may be produced by the $\alpha,3p$ reaction in aluminium. The practical threshold for the reaction is ~35 MeV and the cross-section with 41 MeV α particles is ~0·2 mb.

THERE was until the last few years no convenient magnesium isotope for use in tracer studies. The discovery by SHELINE and JOHNSON[1] of Mg^{28} with a 21·3-hour half-life has made available a tracer which can be very useful for the study of important chemical and biological reactions. The main source of the tracer today is from $\alpha,2p$ or T,p reactions on Mg^{26} (11% abundant), thus making it impossible to obtain carrier-free Mg^{28}. Although very high specific activity Mg^{28} has been prepared by the T,p reaction[2] there are occasions when carrier-free samples would be preferable, if not necessary. It was very interesting to observe therefore that Mg^{28} could be made in reasonable yield from aluminium by an $\alpha,3p$ reaction using the 41 MeV α's from the Brookhaven 60 in. cyclotron. Thus the possibility of obtaining carrier-free Mg^{28} is realized.

Mg^{28} decays by β^- emission to Al^{28}, which is itself unstable, decaying by β^- emission to Si^{28} with a 2·4-min half-life. The observed radiations from the Mg-Al-Si decay chain include a 0·42 MeV and a 2·87 MeV β, and five γ's with energies ranging from 0·03 to 1·78 MeV. SHELINE *et al.*[3] produced the Mg^{28} by an $\alpha,2p$ reaction on Mg^{26} and by a $\gamma,2p$ reaction on Si^{30}. The gamma-ray spectrum from a 100 MeV betatron was required to produce the $\gamma,2p$ reaction on silicon, and the yield was quite low.

The calculated threshold for the $\alpha,3p$ reaction on Al^{27} is ~25 MeV. The height of the coulomb barrier for protons in this region of the Periodic Table is ~3 MeV per proton. If we assume that each proton must have 3 MeV of kinetic energy in order to produce Mg^{28} in any appreciable yield, then ~34 MeV would be the practical threshold. A stacked-foil experiment did indeed show that 35 ± 1 MeV was the minimum α-particle energy which gave sufficient activity to definitely identify Mg^{28}. This energy is well within the range of a 60-in. cyclotron. To determine the absolute cross-section for the $\alpha,3p$ reaction on Al^{27}, a sandwich target of five 1-mil Al foils was bombarded with 41 MeV α's and the beam intensity measured with a Faraday cup. The Al foils were counted on a beta proportional counter of known geometry. Corrections were made for self-absorption and self-scattering in the foil and the multiple β decays in the Mg^{28}-Al^{28}-Si^{28} chain. With 41 MeV α particles, the $\alpha,3p$ cross-section on Al^{27} has a value of ~0·2 mb.

* Research performed under the auspices of the U.S. Atomic Energy Commission.

[1] R. K. SHELINE and N. R. JOHNSON *Phys. Rev.* **89**, 520 (1953).
[2] *BNL* 364(*AS*-9) p. 59. 1 July 1955.
[3] R. K. SHELINE *et. al.* *Phys. Rev.* **94**, 1642 (1954).

The specific activity of a Mg^{28} sample prepared by the $\alpha,3p$ reaction in aluminium depends directly on the magnesium impurity in the target. Very pure aluminium (nominally >99·99%) was used in this work. Spectrographic and neutron activation analysis also indicated <0·01% magnesium impurity. A simple chemical procedure[4] yields a carrier-free Mg^{28} solution free from Al^{+3} ion and Na^{24} activity. Stray neutrons produce Na^{24} by the n,α reaction in Al. The procedure is based on the fact that carrier-free Mg will form a radiocolloid in basic solution and will be held up on a glass frit. A fast and efficient separation (~80% chemical yield) is the following:

1. Dissolve aluminium target in concentrated NaOH.
2. Filter through a fine glass frit.
3. Wash frit with NaOH a few times.
4. Wash frit with H_2O.
5. Dissolve $Mg(OH)_2$ off frit with dilute HCl or HNO_3.

The levels of Mg^{28} activity obtained depend, of course, on the beam intensity and length of bombardment. A relatively short run, 100 μAh on a 1 mil Al target, will give $\sim 1{\cdot}5 \times 10^7$ d/m of Mg^{28} activity at the end of bombardment. On days when targets are irradiated with the external α beam, the aluminium window in the cyclotron through which the α's emerge can be a very good source of Mg^{28}. Care should be taken, however, that aluminium and not an aluminium alloy is used for the window if carrier-free Mg^{28} is desired.

[4] W. M. GARRISON and J. G. HAMILTON *Chem. Rev.* **49**, 237 (1951).

J. Inorg. Nucl. Chem., 1957, Vol. 4, pp. 239 to 244. Pergamon Press Ltd., London

THE ABSOLUTE YIELD OF Cs^{137} IN FAST-NEUTRON FISSION OF U^{235} AND Pu^{239}

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(*Received* 22 *February* 1957)

Abstract—The absolute fission yield of Cs^{137} has been determined for fast-neutron fission of U^{235} and Pu^{239}. The number of fissions was determined by absolute counting of the fission fragments. The Cs^{137} was determined by absolute β counting with an end-window proportional counter. The yields were found to be 6·87 per cent and 7·45 per cent for U^{235} and Pu^{239}, respectively. These values are based on a Cs^{137} half-life of 32·6 years.

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THE absolute fission yield of a long-lived fission product can be used as the basis of a general method for determining the burn-up of reactor fuel. Because of its long half-life and high fission yield, Cs^{137} has been selected for use in burn-up analysis. For fast reactors, therefore, a knowledge of the Cs^{137} yield in fast-neutron fission is useful. Fast-fission yields of this nuclide have not been reported in the literature. We have determined the absolute yield of Cs^{137} in fast-neutron fission of U^{235} and Pu^{239}.

EXPERIMENTAL PROCEDURE

Apparatus

The neutron irradiation was performed in a vertical hole of the Argonne research reactor, CP-5, using a fission counter and uranium converter thimble (Fig. 1) similar to those employed by FREEDMAN and STEINBERG.[1] A light sample of the fissile material weighing 3–6 μg was deposited on a platinum disc and placed 3 mm from the collecting plate of the small ionization chamber which served as the fission counter. P-10 gas (90 per cent argon, 10 per cent methane) was allowed to flow through the chamber. A heavy sample disc of the same fissile species, weighing 1·5–3·8 g, was placed outside the chamber about 1·5 mm from the light sample and coaxial to it.

The converter thimble had a $\frac{1}{4}$ in.-thick layer of uranium containing 10 per cent U^{235}. Inside of this was a layer of boron carbide which was at least $\frac{1}{4}$ in. thick at every point. The ionization chamber was attached to the converter cap, which had a boron carbide filler. The converter and ionization chamber were suspended through a vertical hole in the graphite reflector of the reactor. Attached to the top of the converter was a preamplifier surrounded by a cadmium sheet of 1/32 in. thickness. Above the preamplifier was a graphite block whose purpose was to decrease the number of fast neutrons escaping into the pile room. The whole assembly was insulated electrically from the pile-wall by a Micanite sheet. The counter was grounded only through the cables, which extended about 40 ft to the linear amplifier.

Fig. 2 shows a block diagram of the electronic components. The preamplifier is

[1] M. S. FREEDMAN and E. P. STEINBERG Absolute Fission Yield Experiments. Paper 200 in *Radiochemical Studies: The Fission Products* (Ed. C. D. CORYELL and N. SUGARMAN).

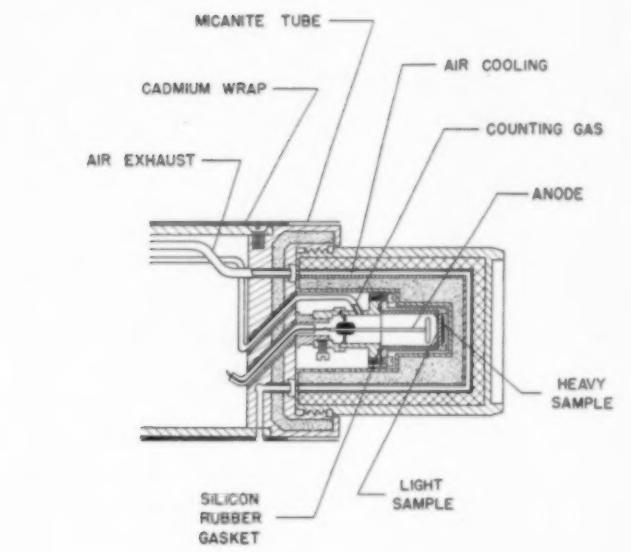

FIG. 1.—Fission counter and converter thimble.

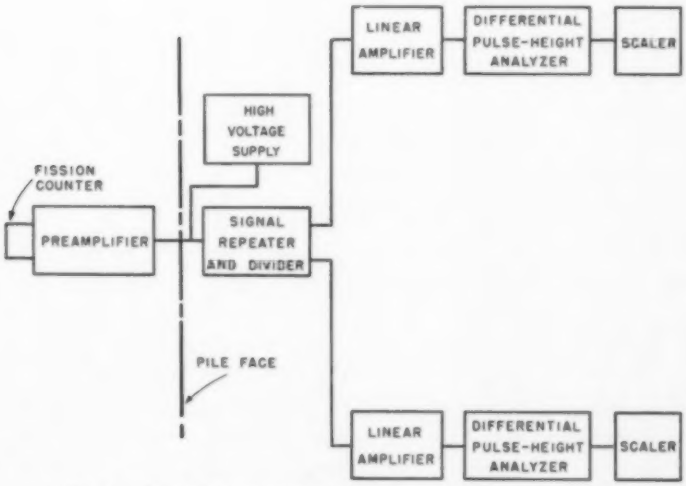

FIG. 2.—Block diagram of electronic components of fission counter.

a non-inverting type with a stabilized gain of 75. The signal repeater and divider is a double-cathode follower capable of driving the long signal cable leading to the linear amplifier (Atomic Instrument Co., model 218). The amplified pulse is fed into an Atomic Instrument Co., model 510 single-channel pulse-height analyser. The signal was divided so that one analyser could scan the pulse array while the other was taking an integrated count. The counts were recorded on a conventional scaler.

Light sample preparations

The light sample of plutonium was prepared by ozone oxidation of a plutonium solution followed by electrodeposition of $Pu(OH)_4$ from basic solution. The deposit was then ignited to PuO_2. The deposit was confined to an area of 1 cm diameter. The isotopic content of the plutonium was determined by mass spectrometry and alpha-pulse analysis; the specific alpha activity was therefore known. The weight of the sample was then determined by low-geometry alpha counting.

The light sample of uranium was prepared by dissolving a weighed amount of enriched uranium of known isotopic content and depositing an aliquot of this solution onto a platinum disc; a drop of glycerol was used as a spreading agent during the evaporation. The sample was ignited, covered with a very thin layer of collodion, and assayed with a 2π alpha counter. The alpha count agreed within 1 per cent with the calculated activity based on the weighing of the uranium and on the isotopic content as determined by mass spectrometry.

Fission-counting procedure

Fig. 3 shows a typical pulse-height spectrum. The pulses to the left of the valley are due to alpha particles and γ-ray pile-up. The pulses to the right of the valley are due to fission fragments. The position of the valley was checked periodically during each run; each irradiation lasted 24–40 hr. In a typical run the analyser was set to integrate all of the fission counts; usually about 40 per cent of these pulses were above the upper end of the analyser pulse-height scale. By having some of the pulses above the scale, it was possible to have a wide valley between the noise and the fission pulses. The background counting rate was negligible. The dimensions of the light sample and the fission chamber were such that one-half of the fission fragments, i.e. one fragment from each fission event, would traverse at least 3 mm of gas. An alpha particle travelling this same distance would dissipate only a small fraction of its energy in the gas, whereas a fission fragment, whose path is short and has its greatest ionization density near its origin, would dissipate a large fraction of its energy in this distance.

If the neutron exposure of the light and heavy samples were equal, then the ratio of the number of fissions occurring in the two samples would be equal to the ratio of their masses. But since the heavy sample would shadow the light sample by removing some of the neutrons approaching from one direction, the ratio of heavy-sample exposure to light-sample exposure would be greater than the ratio of sample masses. In order to correct for the shadowing effect, the flux was monitored with thin copper foils placed on each face of the heavy disc and under the light-sample disc. The relative neutron exposure of the copper foils was determined by measuring the 12·8 hr Cu^{64} activity induced in each foil. The shadowing correction was about 4 per cent in each case.

Chemical separations

About 4 months after the irradiation the heavy samples, which had been wrapped in aluminium or nickel, were dissolved, along with their aluminium or nickel wrapper, in nitric acid, and the solutions were diluted to 100 ml. Aliquots of these solutions were then used for Cs^{137} analysis. After addition of cesium carrier to the solution, the cesium was precipitated as the perchlorate; this was then dissolved and the

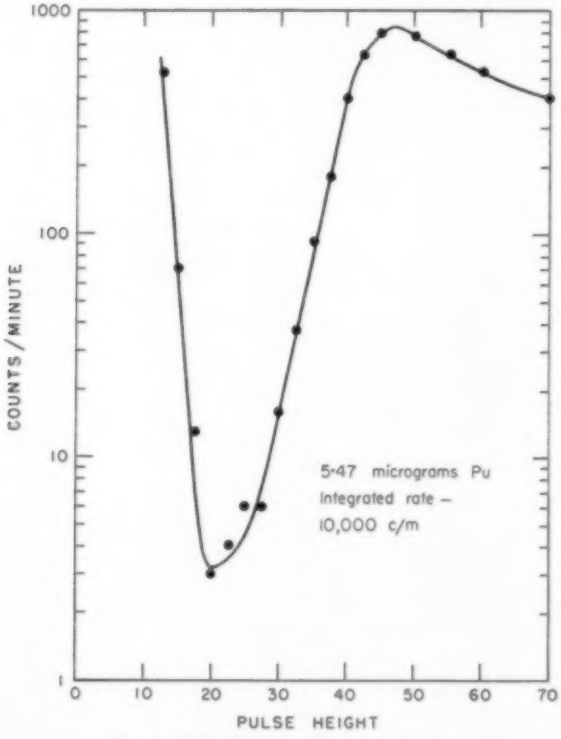

FIG. 3.—Distribution of fission-fragment pulses.

solution was scavenged three times by hydrous ferric oxide precipitation. Cesium perchlorate was again precipitated and mounted on a glass fibre filter disc for β counting. The plutonium solutions were passed through a cation exchange column to remove plutonium before the cesium separation.

Cs^{137} beta counting

A solution of carrier-free Cs^{137} was assayed with a 4π β counter, a correction being applied for the conversion of γ-rays from the Ba^{137m} daughter. The branching ratio was taken to be 92 per cent to Ba^{137m} and 8 per cent to Ba^{137} ground state.[2] The conversion coefficient was taken to be 11·8 per cent.[3,4] This solution was then used to calibrate the end-window proportional counter for counting the radiation of

[2] L. M. LANGER and R. D. MOFFAT *Phys. Rev.* **82**, 635 (1951).
[3] M. A. WAGGONER *Phys. Rev.* **82**, 906 (1951).
[4] G. A. GRAVES, L. M. LANGER, and R. D. MOFFAT *Phys. Rev.* **88**, 344 (1952).

this nuclide. The counting efficiency was determined as a function of sample thickness. By means of this efficiency factor the absolute disintegration rate of the samples was determined. The disintegration rate was converted to the equivalent number of Cs^{137} atoms present in each sample by means of the half-life value of 32·6 years.[5] The β counting was done about eight months after the irradiation. The Cs^{136} activity of the samples was, therefore, negligible. Since the burn-up was very low ($\sim 10^{-8}$ per cent), the Cs^{134} activity built up from neutron capture by fission product Cs^{133} would also be negligible.

RESULTS AND DISCUSSION

Two uranium samples and five plutonium samples were irradiated. The plutonium samples were of two different isotopic compositions, one of low Pu^{240} content (designated by letters in Table 2) and one of Hanford level (designated by numbers in Table 2); there was no significant difference in the Cs^{137} yield from the two types of samples. The U^{235} samples contained 93 per cent U^{235}. The U^{234} and U^{238} in these samples contributed less than 1 per cent of the fissions.

The results of the Cs^{137} fission-yield determinations are shown in Table 1 for U^{235}

TABLE 1.—YIELD OF Cs^{137} IN FAST-NEUTRON FISSION OF U^{235}

Sample No.	Ratio of heavy-sample mass to light-sample mass	Shadow factor	Number of fissions in light sample	Number of fissions in heavy sample	Aliquot No.	Zero time Cs^{137} activity (d.p.m./ total sample)	Number of Cs^{137} atoms in sample*	Fission yield (per cent)
10-M	$0{\cdot}8396 \times 10^6$	1·039	$17{\cdot}64 \times 10^6$	$15{\cdot}39 \times 10^{12}$	1A	42,810	$1{\cdot}059 \times 10^{12}$	6·88
					1B	42,740	1·057	6·86
					2A	42,510	1·052	6·84
					2B	42,310	1·047	6·80
					3A	41,570	1·028	6·68
						Average		6·81
10	$0{\cdot}8961 \times 10^6$	1·042	$15{\cdot}03 \times 10^6$	$14{\cdot}03 \times 10^{12}$	1A	39,340	$0{\cdot}973 \times 10^{12}$	6·94
					1B	39,820	0·985	7·02
					2A	39,120	0·968	6·90
					2B	39,850	0·986	7·03
					2C	39,030	0·966	6·89
					3A	38,560	0·954	6·80
					3B	39,460	0·976	6·96
						Average		6·93
	Overall average yield = 6·87 ± 0·17%							

* The number of atoms was calculated on the basis of Cs^{137} half-life = 32·6 years.

and in Table 2 for Pu^{239}. These yields are greater than the yields reported in the literature for thermal neutron fission of these nuclides: 5·9 per cent[6] for U^{235} (mass spectrometric); 5·8 per cent[6] (radiometric) and 4·94 per cent[7] (mass spectrometric) for Pu^{239}. These thermal values are relative yield determinations. The radiometric value is based on a 33 yr Cs^{137} half-life; the mass spectrometric values are nearly independent of the half-life value used. Although the reported yield values for thermal neutron fission of Pu^{239} vary widely, they are all much lower than our value of 7·45 per cent. If the Cs^{137} yield is sensitive to neutron energy, then this

[5] E. P. STEINBERG, L. E. GLENDENIN, and K. F. FLYNN Private communication.
[6] E. P. STEINBERG and L. E. GLENDENIN Survey of Radiochemical Studies of the Fission Process. P/614 *Peaceful Uses of Atomic Energy* Vol. 7.
[7] D. M. WILES, J. A. PETRUSKA, and R. H. TOMLINSON *Canad. J. Chem.* **34**, 227 (1956).

TABLE 2.—YIELD OF Cs^{137} IN FAST-NEUTRON FISSION OF Pu^{239}

Sample No.	Ratio of heavy-sample mass to light-sample mass	Shadow factor	Number of fissions in light sample	Number of fissions in heavy sample	Aliquot No.	Zero time Cs^{137} activity (d.p.m./ total sample)	Number of Cs^{137} atoms in sample*	Fission yield (per cent)
3	$0{\cdot}4892 \times 10^6$	1·043	$24{\cdot}73 \times 10^6$	$12{\cdot}62 \times 10^{12}$	1	39,170	$0{\cdot}9691 \times 10^{12}$	7·68
					2	37,990	0·9399	7·45
					3	38,560	0·9540	7·56
					4A	38,800	0·9599	7·61
					4B	38,180	0·9446	7·49
						Average		7·56
4	$0{\cdot}2612 \times 10^6$	1·043	$38{\cdot}93 \times 10^6$	$10{\cdot}61 \times 10^{12}$	2	31,220	$0{\cdot}7724 \times 10^{12}$	7·28
					4	31,280	0·7739	7·30
						Average		7·29
5	$0{\cdot}2627 \times 10^6$	1·043	$47{\cdot}61 \times 10^6$	$13{\cdot}05 \times 10^{12}$	1	38,340	$0{\cdot}9485 \times 10^{12}$	7·27
					2	38,360	0·9490	7·28
						Average		7·275
C	$0{\cdot}4441 \times 10^6$	1·044	$26{\cdot}25 \times 10^6$	$12{\cdot}17 \times 10^{12}$	1	36,810	$0{\cdot}910 \times 10^{12}$	7·48
					2	37,180	0·9198	7·56
					3	36,670	0·9072	7·45
					4	36,890	0·9127	7·50
						Average		7·50
E	$0{\cdot}4261 \times 10^6$	1·042	$25{\cdot}82 \times 10^6$	$11{\cdot}46 \times 10^{12}$	1	34,360	$0{\cdot}8501 \times 10^{12}$	7·42
					2	34,980	0·8654	7·55
					3	34,490	0·8533	7·45
					4	34,280	0·8481	7·40
						Average		7·45
	Overall average yield = 7·45 ± 0·20%							

* The number of atoms was calculated on the basis of Cs^{137} half-life = 32·6 years.

difference could be real. The neutron-energy spectrum in our experiments is essentially a fission-neutron spectrum with some of the lower-energy neutrons removed by the boron carbide blanket in the converter thimble.

In the radiometric determination of a fission yield, the number of fission-product atoms is calculated from the measured disintegration rate of a sample of the particular fission-product species. Thus, the yield will be proportional to the half-life value which is used in the calculation. In the case of Cs^{137}, the reported half-life values are $32{\cdot}6 \pm 2$ yr,[5] $30{\cdot}0^{+0{\cdot}3}_{-0{\cdot}4}$ yr,[8] and $26{\cdot}6 \pm 0{\cdot}4$ yr.[9] If the half-life is actually lower than the value we have used above (32·6 yr), then our yield values should be lowered proportionately. Thus, if the average of the three half-life values quoted above is used (29·7 yr), our yield values become $6{\cdot}2_6$ per cent for U^{235} fission and $6{\cdot}7_9$ per cent for Pu^{239} fission.

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THE VALENCE STATES OF THE ELEMENTS V, Cr, Mn, Fe, Co, Ni, and Cu

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Abstract—Empirical atomic spectral parameters are obtained for various electronic configurations of the atoms in the period from V to Cu, and the excitation energies required to achieve some of the valence states of these atoms are calculated. Electronegativity values (as defined by MULLIKEN) are obtained for Ni and Cu. From the valence-state ionization potentials, it is concluded that the electronegativity property increases for a given atom of this period in passing from the valence states $d^n \rightarrow d^{n-1}s \rightarrow d^{n-2}s^2$.

The relative instability of the compounds of these metals deriving from the higher valence states of high co-ordination number is discussed in relation to valence-state excitation energies. The covalent nature of the metal di*cyclo*pentadienyl derivatives is examined in relation to the d_π valence-state ionization potentials.

IN an earlier paper,[1] some calculations were made on the valence-state excitation energies of a number of elements from Groups 2, 3, and 4 of the Periodic Table. The present work extends to the third-row sub-group A elements V, Cr, and Mn, to the transition elements Fe, Co, and Ni, and to Cu. All the observed valence-shell configurations in these elements belong to the general description $3d^q4s^m4p^n$, ($m \leqslant 2$, $n \leqslant 6$, and $q \leqslant 10$, but also $\geqslant 3$), so that we are here concerned primarily with *d*-orbital containing configurations.

The valence-state excitation energies were derived on the basis of the Slater-Condon theory of atomic spectra,[2] and the definition by VAN VLECK[3] of a "valence state." Evaluation of the unknown parameters (*F*'s and *G*'s) occurring in SLATER's equations was made by least-squares fitting of the equations to the appropriate spectroscopic energy levels, using empirical data given by MOORE.[4] RACAH[5] has derived the equations of interest to us in an economical form, and it is RACAH's symbolism that is used here.

The calculations of the Slater-Condon parameters by means of least-squares* were made using the Manchester University computing machine. The theoretical formulae[5] were compared with the experimental term values, not, however, taking configuration interactions into account. The results of these computations are given in the first part of the paper; later, we have derived (or estimated) some valence-state excitation energies of interest, and used them in discussing the character of the bonding orbitals employed by these elements.

* The parameters given in Tables 2, 3, and 4 were calculated using an approximation to the exact "least-squares" method, in order to reduce the length of the computations. The fit by least-squares was made giving a weight of unity for each term.

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1. EVALUATION OF PARAMETER VALUES

a. *V(I) and Cr(II).* SCHWEIZER[6] has made a least-squares fit with RACAH's formulae of the known spectroscopic terms belonging to d^3s^2, d^4s, and d^5 in V(I) and Cr(II), obtaining the values (in cm^{-1}) given in Table 1. Column I derives from terms belonging to d^3s^2 only, and column II from terms belonging to d^4s. Column III was obtained from the best fit of all terms from both d^3s^2 and d^4s, and column IV similarly, but with correction for configuration interactions.

TABLE 1.—PARAMETER VALUES IN V(I), Cr(II) (SCHWEIZER)

	V(I)				Cr(II)	
	I	II	III	IV	III	IV
$A(d^3s^2)$	9757	—	10269	10443	(55000)†	
$A(d^4s)$	—	19664	19025	19202	35211	35192
$A(d^5)$	—	—	(40432)*	(40537)*	23579	23317
B	632	582	578	581	720	710
C	2654	2108	2273	2244	2778	2790
G_2	—	1305	1307	1332	1459	1531

$$A(d^3s^2) = F_0(s:s) + 6F_0(s:d) + 3A - 3G_2$$
$$A(d^4s) = 4F_0(s:d) + 6A$$
$$A(d^5) = 10A$$
$$A = F_0(d:d) - 49F_4(d:d)$$
$$B = F_2(d:d) - 5F_4(d:d)$$
$$C = 35F_4(d:d)$$

* From ^6S, d^5.
† From ^2G, ^4P, and ^2P, d^3s^2, given in MOORE's tables. These terms have not been assigned with certainty.

The spectrum of Mn(III) contains two terms that have been identified as belonging to d^4s, and five terms from d^5. Least-squares fitting of the d^5 terms gave $A(d^5) = 33338$, $B = 947$, $C = 3248$. Retaining the B value, the d^4s terms then require $A(d^4s) = 89978$, and $G_2 = 1786$.

b. *Cr(I), Mn(II), Fe(III).* The configurations of importance in the spectrum of Cr(I) are d^4s^2, d^5s, d^4sp, and d^5p. Only one term, ^5D, belonging to d^6 has been found. Several terms from d^6 have been located in the spectra of Mn(II) and Fe(III), but none from d^4s^2 (apart from ^5D in Mn(II)) have been found. Terms from d^4sp have not been located in Fe(III). We have fitted the known terms belonging to d^4s^2, d^5s, and d^6 in the Cr(I) spectrum to RACAH's formulae, obtaining the parameter values given in Table 2. This table includes parameter values obtained by TREES,[7] from the terms belonging to d^5s and d^6 in Mn(II) and Fe(III). We have checked TREES' calculations in the case of Mn(II), d^6. The sensitivity of the least-squares method to small changes in the parameters is, however, not very high: TREES gives $A(d^6) = 30948{\cdot}3$, $B = 762{\cdot}85$, $C = 2904{\cdot}6$, whilst we find that the values of $A = 30938$, $B = 762{\cdot}49$, $C = 2096{\cdot}6$ are as good as those of TREES in respect of the root-mean-square deviation (946 cm^{-1}), and slightly better in respect of the arithmetic sum of the individual errors (+2 against −14). The terms d^4s^2 and d^5s of Cr(I) were fitted separately, and also as a group.

[6] A. A. SCHWEIZER *Phys. Rev.* **80**, 1080 (1950).
[7] R. F. TREES *Phys. Rev.* **82**, 683 (1951); **83**, 756 (1951); **84**, 1089 (1951).

TABLE 2.—PARAMETER VALUES IN Cr(I), Mn(II), AND Fe(III)

	A	B	C	G_2	Number of terms
Cr(I), d^4s^2	26918	902·6	2955	—	8
Cr(I), d^5s	21708	597·5	2505	1318	19
Cr(I), d^4s^2	24506	637	2558	1407	27
d^5s	28096				
Cr(I), d^6	(48875)	637	2558		1
Mn(II), d^4s^2	(76364)	1000[a]	3200[a]	—	1
Mn(II), d^5s	40376	921	3138	1605	9
Mn(II), d^6	30948	763	2905	—	6
Fe(III), d^5s	75351	1030	4107	1831	26
Fe(III), d^6	20354	937	3722	—	14

$$A(d^4s^2) = F_0(s:s) + 8F_0(s:d) + 6A - 4G_2$$
$$A(d^5s) = 5F_0(s:d) + 10A$$
$$A(d^6) = 15A - 14B + 7C$$

r.m.s. deviations; Cr(I), $d^4s^2 = 579\ \text{cm}^{-1}$; $d^5s = 1095\ \text{cm}^{-1}$; $(d^4s^2 + d^5s) = 1346\ \text{cm}^{-1}$

The parameters superscripted *a* are *assumed* values.

TABLE 3.—PARAMETER VALUES IN Mn(I), Fe(II), AND Co(III)

	A	B	C	G_2	Number of terms
Mn(I), d^5s^2	26697				4
Mn(I), d^6s	37157	720	3087	1287	8
Mn(I), d^7	53780				2
Fe(II), d^5s^2	55780				2
Fe(II), d^6s	25626	869	3638	1589	22
Fe(II), d^7	13540				8
Co(III), d^6s	78554	1115	4366	2073	11
Co(III), d^7	16118				5

$$A(d^5s^2) = F_0(s:s) + 10F_0(s:d) + 10A - 5G_2$$
$$A(d^6s) = 6F_0(s:d) + 15A - 14B + 7C - G_2$$
$$A(d^7) = 21A - 28B + 14C$$

r.m.s. deviations; Mn(I) = 1182 cm^{-1}; Fe(II) = 1150 cm^{-1}; Co(III) = 993 cm^{-1}.

c. *Mn(I), Fe(II), and Co(III).* The configuration of interest in the spectrum of Mn(I) are d^5s^2, d^5sp, d^5p^2, d^6s, d^6p, and d^7; only one term from d^5p^2 and two from d^7 have been identified. The spectrum of Fe(II) contains terms from d^7, d^6s, d^6p, d^5sp, and two terms from d^5s^2. In Co(III), terms from d^7, d^6s, and d^6p are known.

d. *Fe(I), Co(II), and Ni(III).* Numerous terms belonging to d^6s^2, d^6sp, d^7s, and d^7p have been located in the Fe(I) spectrum; there are two terms from d^5s^2p, and one term from d^8. In Co(II), only one term from d^6s^2 is known, and two from d^8 but there

TABLE 4.—PARAMETER VALUES IN Fe(I), Co(II), AND Ni(III)

	A	B	C	G_2	Number of terms
Fe(I), d^6s^2	18561				9
Fe(I), d^7s	22317	806	3506	1314	14
Fe(I), d^8	39713				1
Co(II), d^6s^2	(62257)	1000[a]	4000[a]		1
Co(II), d^7s	22708	932	3828	1579	6
Co(II), d^8	7440	843	3800[a]		2
Ni(III), d^7s	77142	1112	4831	1906	5
Ni(III), d^8	9442	1056	4800[a]	—	2

$$A(d^6s^2) = F_0(s:s) + 12F_0(s:d) + 15A - 14B + 7C - 6G_2$$
$$A(d^7s) = 7F_0(s:d) + 21A - 28B + 14C - 2G_2$$
$$A(d^8) = 28A - 42B + 21C$$

r.m.s. deviations: Fe(I) = 1002 cm^{-1}; Co(II), d^7s = 284 cm^{-1}; Ni(III), d^7s = 84 cm^{-1}.

are several belonging to d^6sp, d^7s, and d^7p. The Ni(III) spectrum contains terms from d^8, d^7s, and d^7p. Terms from Fe(I) were fitted as a set, and from Co(II) and Ni(III) separately.

e. *Co(I), Ni(II), Cu(III).* Terms belonging to d^9, d^8s, and d^8p occur in the spectra of each member of this group. In the spectrum of Co(I), terms belonging to d^7s^2 and d^7sp have also been identified. An analysis of the terms from d^7s^2 and d^8s in Co(I) has been given by RACAH,[8] who has also[5] derived the parameter values for the configuration d^8p in Ni(II). RACAH's values are included in Table 5.

TABLE 5.—PARAMETER VALUES IN Co(I), Ni(II), Cu(III)

	A	B	C	G_2	F_2	G_1	G_3
Co(I), d^7s^2	13444						
		798	4167	1128	—	—	—
Co(I), d^8s	12430						
Ni(II), d^8s	20709	1049	4118	1523			
d^8p	62247	1022	4509	—	364	303	54·4
Cu(III), d^8s	75553	1238	4659	1829	—	—	—

$$A(d^7s^2) = F_0(s:s) + 14F_0(s:d) + 21A - 28B + 14C - 7G_2$$
$$A(d^8s) = 8F_0(s:d) + 28A - 42B + 21C - 3G_2$$
$$A(d^8p) = 28A - 42B + 21C + 8F_0(p:d) - 10G_1 - 35G_3$$

r.m.s. deviations: Ni(II), d^8s = 552 cm^{-1}; Cu(III), d^8s = 639 cm^{-1};

f. *Ni(I), Cu(II), Zn(III).* Terms belonging to d^{10}, d^9s, d^9p, and d^8sp have been located for each member of this group. Terms from d^8s^2 have not yet been found in the spectrum of Zn(III), but have been observed in both Ni(I) and Cu(II). The parameter values from d^8s^2 and d^9p are given in Table 6.

[8] G. RACAH *Phys. Rev.* **61**, 537 (1942).

TABLE 6.—PARAMETER VALUES IN Ni(I), Cu(II), AND Zn(III)

	A	B	C	F_2	G_1	G_3
Ni(I), d^8s^2	8847	1025	4226			
d^9p	29901	—	—	117	195	45
Cu(II), d^9s^2	80380	1216	4745	—	—	—
d^9p	69786	—	—	376	322	96
Zn(III), d^9p	142729	—	—	554	433	144

$$A(d^8s^2) = F_0(s:s) + 16F_0(s:d) + 28A - 42B + 21C - 8G_2$$
$$A(d^9p) = 9F_0(d:p) + 36A - 56B + 28C - 10G_1 - 35G_2$$
$$G_3 = 3/245G^2(p:d)$$

r.m.s. deviations: Ni(I). $d^8s^2 = 548\ \text{cm}^{-1}$; $d^9p = 419\ \text{cm}^{-1}$; Cu(II), $d^9s^2 = 649\ \text{cm}^{-1}$; $d^9p = 532\ \text{cm}^{-1}$; Zn(III), $d^9p = 915\ \text{cm}^{-1}$.

Three other previous determinations of atomic spectral parameters, less detailed than those given here, have been made by CATALAN, ROHRLICH, and SHENSTONE,[9] by ORGEL,[10] and by TANAHE and SUGANO.[11]

2. VALENCE-STATE ENERGIES

The valence-state formulae given below were obtained by the same procedure as that of VAN VLECK[3] in his discussion of the valence states of the carbon atom. In dealing with the various hybrid orbitals built up from s-, p-, and d-electrons, HULTGREN's treatment[12] proved valuable. The symbolism adopted to describe configurations and orbital wave-functions in detail is:

$$x = p_x; \qquad y = p_y; \qquad z = p_z;$$
$$\sigma = d_{z^2}; \qquad \pi = d_{xz}; \qquad \pi' = d_{yz};$$
$$\delta = d_{x^2-y^2}; \qquad \delta' = d_{xy}$$

The symbol V_n describes the valence state of an atom in which the n bonding electrons are assigned indeterminate spin. The values given under "strength" refer to the bonding-power of the orbitals in the sense in which this measure is used by PAULING[13] and HULTGREN.[12]

d^n bonds

(i) V_2, d^2, *or* d^8.

Symmetry: C_{2v} ($\theta = 0°$ and $125° 16'$; $\phi = 0°$).

Orbitals: $\psi_1 = \sigma$; $\psi_2 = \sqrt{\frac{2}{3}}\pi - \sqrt{\frac{1}{3}}\delta$.

Strength: 2·236.

Valence-state formulae: $A(d^2, \text{or } d^8) - B + \frac{1}{2}C$.

[9] M. A. CATALAN, F. ROHRLICH, and A. G. SHENSTONE *Proc. roy. Soc.* **A221**, 421 (1954).
[10] L. E. ORGEL *J. chem. Phys.* **23**, 1819 (1955).
[11] Y. TANABE and S. SUGANO *J. phys. Soc. Japan* **9**, 753, 766 (1954).
[12] R. HULTGREN *Phys. Rev.* **40**, 891 (1932).
[13] L. PAULING *J. Amer. chem. Soc.* **53**, 1367 (1931).

(ii) V_3, d^3 *or* d^7.

Symmetry: D_{3h} ($\theta = 90°$; $\phi = 0°$, 120°, 240°).

Orbitals: $\psi_1 = -\sqrt{\tfrac{1}{3}}\,\sigma + \sqrt{\tfrac{2}{3}}\,\delta$;

$$\psi_{2,3} = -\sqrt{\tfrac{1}{3}}\,\sigma - \sqrt{\tfrac{1}{6}}\,\delta \pm \sqrt{\tfrac{1}{2}}\,\delta'.$$

Strength: 2·227.

Valence-state formulae: $A(d^3, \text{ or } d^7) - 8B + \tfrac{3}{2}C$.

(iii) V_4, d^4 *or* d^6.

Symmetry: C_{4v} ($\theta = 113°$; $\phi = 45°$, 135°, 225°, 315°).

Orbitals: $\psi_1 = -\tfrac{1}{2}\sigma - \tfrac{1}{2}\pi - \tfrac{1}{2}\pi' + \tfrac{1}{2}\delta'$;

$$\psi_2 = -\tfrac{1}{2}\sigma + \tfrac{1}{2}\pi - \tfrac{1}{2}\pi' - \tfrac{1}{2}\delta, \text{ etc.}$$

Strength: 2·108.

Valence-state formulae: $A(d^4, \text{ or } d^6) - 13{\cdot}5B + 3C$.

(iv) V_5, d^5.

Symmetry: C_{5v} ($\theta = 110° 59'$; $\phi = 0°$, 72°, 144°, 216°, 288°).

Orbitals: $\psi_1 = -\sqrt{\tfrac{1}{5}}\,\sigma - \sqrt{\tfrac{2}{5}}\,(\pi - \delta)$;

$$\psi_2 = -\sqrt{\tfrac{1}{5}}\,\sigma - \sqrt{\tfrac{3}{5}}\,(0{\cdot}309\pi + 0{\cdot}9511\pi' - 0{\cdot}809\delta + 0{\cdot}5878\delta').$$

Strength: 2·194.

Valence-state formulae: $A(d^5) - 22{\cdot}5B + 5C$.

$d^n s$ bonds

(i) V_2, *ds, or* $d^9 s$.

Symmetry: C_{2v} ($\theta = 45°$ and 135°, $\phi = 90°$).

Orbitals: $\sqrt{\tfrac{1}{2}}\,(s \pm \pi')$.

Strength: 2·076.

Valence-state formula:

$$V_2, ds = F_0(s:d) + \tfrac{1}{2}B + \tfrac{1}{5}C - G_2 + \tfrac{1}{8}\Delta_0$$

$$V_2, d^9 s = {}^3D, d^9 s + \tfrac{1}{2}B + \tfrac{1}{5}C + \tfrac{1}{8}\Delta_o$$

$$\Delta_0 = [(F_0(s:s) - 2F_0(s:d) + F_0(d:d)]$$

$$\Delta_0(ds) = F_0(d:d) + {}^1S, s^2 - {}^3D, ds - {}^1D, ds$$

$$\Delta_0(d^9 s) = A(d^8 s^2) + \tfrac{7}{5}C + {}^1S, d^{10} - {}^3D, d^9 s - {}^1D, d^9 s.$$

(ii) V_3, d^2s, *or* d^8s.

Symmetry: D_{3h} ($\theta = 90°$, $\phi = 0°$, 120°, 240°).

Orbitals: $\psi_1 = \sqrt{\tfrac{1}{3}}\, s + \sqrt{\tfrac{2}{3}}\, \delta$; $\psi_{2,3} = \sqrt{\tfrac{1}{3}}\, s - \sqrt{\tfrac{1}{6}}\, \delta \pm \sqrt{\tfrac{1}{2}}\, \delta'$.

Strength: 2·158.

Valence-state formulae: $A(d^2s, \text{ or } d^8s) + 4\tfrac{2}{3}B + \tfrac{23}{30}C - \tfrac{5}{3}G_2 + \tfrac{1}{6}\Delta_0$.

$$\Delta_0\,(d^2s) = A(d^3) - 2A(d^2s) + \tfrac{7}{5}C + G_2 + {}^2D,\ ds^2.$$

$$\Delta_0\,(d^8s) = A(d^7s^2) - 2A(d^8s) + \tfrac{7}{5}C + G_2 + {}^2D,\ d^9.$$

$$A(d^3) = 3A;\ A(d^2s) = 2F_0\,(s:d) + A.$$

(iii) V_4, d^3s, *or* d^7s.

Symmetry: T_d ($\theta = 54°\,44'$ and $125°\,16'$; $\phi = 45°$, 135°, 225°, 315°).

Orbitals: $\psi_1 = \tfrac{1}{2}(s + \pi + \pi' + \delta')$

$\psi_2 = \tfrac{1}{2}(s - \pi - \pi' + \delta')$, etc.

Strength: 2·437.

Valence-state formula: $A(d^3s \text{ or } d^7s) - 9\tfrac{3}{4}B + 1\tfrac{4}{5}C - 2\tfrac{1}{4}G_2 + 1\tfrac{3}{16}\Delta_0$

$$\Delta_0(d^3s) = A(d^4) + A(d^2s^2) - 2A(d^3s) + \tfrac{7}{5}C + 2G_2$$

$$\Delta_0(d^7s) = A(d^8) + A(d^6s^2) - 2A(d^7s) + \tfrac{7}{5}C + 2G_2$$

$$A(d^4) = 6A;\ A(d^3s) = 3F_0(s:d) + 3A;$$

$$A(d^2s^2) = F_0(s:s) + 4F_0(s:d) + A - 2G_2.$$

(iv) V_5, d^4s *or* d^6s.

Symmetry: C_{4v} ($\theta = 0°$ and various; $\phi = 45°$, 135°, 225°, 315°).

Orbitals: $\psi_1 = \sin\alpha\, s + \cos\alpha\, \sigma$

$\psi_2 = \tfrac{1}{2}\cos\alpha s - \tfrac{1}{2}\sin\alpha\,\sigma - \tfrac{1}{2}\pi - \tfrac{1}{2}\pi' + \tfrac{1}{2}\delta'$

$\psi_3 = \tfrac{1}{2}\cos\alpha s - \tfrac{1}{2}\sin\alpha\,\sigma + \tfrac{1}{2}\pi - \tfrac{1}{2}\pi' - \tfrac{1}{2}\delta'$ etc.

Valence-state formula: $(1\tfrac{3}{16}\cos^4\alpha + \tfrac{1}{2}\sin^2\alpha\cos^2\alpha)\,\Delta_0 + 4F_0(s:d)$

$+ 6F_0(d:d) - 12\tfrac{3}{4}F_2 + \tfrac{1}{4}\sin^2\alpha\,(5\cos^2\alpha - 3)\,F_2 - 194\tfrac{1}{4}F_4$

$+ \sin^2\alpha\,(84 - 11\tfrac{1}{4}\sin^2\alpha)\,F_4 - 2G_2 - \tfrac{1}{4}\cos^2\alpha\,(5\sin^2\alpha + 3)G_2$

[For particular case, $\sin\alpha = \frac{1}{\sqrt{5}}$, $\cos\alpha = \frac{2}{\sqrt{5}}$, $\theta = 0°$ and $118°\,57'$,

Strength: $= 2{\cdot}447$ (one bond), 2·427 (four bonds)

Valence-state formula $= \tfrac{1}{5}\Delta_0 + A(d^4s) - 12{\cdot}7B + 1{\cdot}53C - 2{\cdot}8G_2$]

$$\Delta_0(d^4s) = A(d^3s^2) + A(d^5) - 2A(d^4s) + \tfrac{7}{5}C + 3G_2$$

$$\Delta_0(d^6s) = A(d^5s^2) + A(d^7) - 2A(d^6s) + \tfrac{7}{5}C + 3G_2$$

(v) V_6, d^5s.

Symmetry: C_{5v} ($\theta = 0°$, 116° 34′; $\phi = 0°$, 72°, 144°, 216°, 288°).

Orbitals: $\psi_1 = \frac{1}{\sqrt{6}}s + \sqrt{\frac{5}{6}}\,\sigma$

$\psi_2 = \frac{1}{\sqrt{6}}s - \frac{1}{\sqrt{30}}\sigma - \sqrt{\frac{5}{6}}\,\pi + \sqrt{\frac{5}{6}}\,\delta$, etc.

Strength: 2·449

Valence-state formula: $A(d^5s) - 21\frac{2}{3}B + 5\frac{1}{3}C - 3\frac{1}{3}G_2 + \frac{5}{24}\Delta_0$

$\Delta_0(d^5s) = A(d^4s^2) + A(d^6) - 2A(d^5s) + 14B - 5\frac{2}{3}C + 4G_2$.

d^np bonds

(i) V_2, *dp, or* d^9p.

Symmetry: $D_{\infty h}$

Orbitals: $\psi_{1,2} = \frac{1}{\sqrt{2}}(\sigma \pm z)$

Strength: 2·806

Valence-state formula:

$$V_2, dp = F_0(p:d) + 4F_2(p:d) - 4G_1 - 9G_3 + \tfrac{9}{70}C + \tfrac{1}{6}\Delta_0 + \tfrac{1}{2}\Delta_2$$

$$\Delta_0 = [F_0(p:p) - 2F_0(p:d) + F_0(d:d)]$$

$$\Delta_2 = [F_2(p:p) - 2F_2(p:d) + F_2(d:d)]$$

$$V_2, d^9p = A(d^9p) - 4F_2(p:d) + \tfrac{9}{70}C + \tfrac{1}{6}\Delta_0 + \tfrac{1}{2}\Delta_2.$$

(ii) V_3, d^2p, *or* d^8p.

Symmetry: C_{3v} ($\theta = 54° 44′$; $\phi = 0°$, 120°, 240°).

Orbitals: $\psi_1 = \frac{1}{\sqrt{3}}z + \frac{2}{3}\pi + \frac{\sqrt{2}}{3}\delta$.

$\psi_{2,3} = \frac{1}{\sqrt{3}}z - \frac{1}{3}\pi \pm \frac{1}{\sqrt{3}}\pi' - s\frac{1}{\sqrt{2}}\delta \pm \frac{1}{\sqrt{6}}\delta'$

Strength: 2·403

Valence-state formula:

$$V_3, d^2p = A(d^2p) + \tfrac{2}{5}F_2(p:p) - 2B + \tfrac{23}{35}C - 3\tfrac{1}{3}G_1 - 11\tfrac{2}{3}G_3 + \tfrac{1}{6}\Delta_0$$

$$A(d^2p) = A + 2F_0(p:d)$$

$$V_3, d^8p = A(d^8p) + \tfrac{2}{5}F_2(p:p) - 2B + \tfrac{23}{35}C + \tfrac{2}{5}G_1 + 2\tfrac{1}{2}G_3 + \tfrac{1}{6}\Delta_0.$$

(iii) V_3, d^2p.

Symmetry: C_{3v} ($\theta = 37° 53′$; $\phi = 0°$, 120°, 240°).

Orbitals:

$$\psi_1 = 0{\cdot}4556z + 0{\cdot}3546x + 0{\cdot}3546\sigma + 0{\cdot}2667\delta + 0{\cdot}6854\pi.$$

$$\psi_{2,3} = 0{\cdot}4556z - 0{\cdot}1773x \pm 0{\cdot}3071y + 0{\cdot}3546\sigma - 0{\cdot}1333\delta$$
$$\mp 0{\cdot}2310\delta' - 0{\cdot}3427\,\pi \pm 0{\cdot}5936\pi'.$$

Strength: 2·826.

Valence-state formula:

$$V_3, d^2p = A(d^2p) - 0{\cdot}8209\ F_2(p:p) - 0{\cdot}9065\ F_2(p:d) - 2{\cdot}9065B + 0{\cdot}3068C - 1{\cdot}798G_1 - 6{\cdot}074G_3 + 0{\cdot}3019\ \Delta_0.$$

$d^n sp$ bonds

(i) *V_3, dsp, or d^9sp.*

Symmetry: C_{2v} ($\theta = 0°, 180°, 90°$).

Orbitals: $\psi_{1,2} = \sqrt{\frac{1}{12}}s \pm \sqrt{\frac{1}{2}}z + \sqrt{\frac{5}{12}}\sigma$

$\psi_3 = \sqrt{\frac{5}{6}}s - \sqrt{\frac{1}{6}}\sigma$

Strength: 2·957 (2 bonds), and 1·374 (1 bond)

Valence-state formula:

$$V_3, dsp = F_0(s:p) + F_0(s:d) + F_0(p:d) + \tfrac{1}{12}F_2(p:p) + 4F_2(p:d) + \tfrac{5}{24}B + \tfrac{4}{21}C - \tfrac{7}{12}G_p - \tfrac{17}{84}G_d - 3\tfrac{3}{8}G_1 - 7\tfrac{13}{12}G_3 + \tfrac{1}{48}\Delta_0(s:p) + \tfrac{5}{96}\Delta_0(s:d) + \tfrac{5}{48}\Delta_0(p:d) + \tfrac{5}{12}\Delta_2(p:d)$$

$$V_3, d^9sp = A(d^9sp) + \tfrac{1}{12}F_2(p:p) - 4F_2(p:d) + \tfrac{5}{24}B + \tfrac{4}{21}C - \tfrac{7}{12}G_p + \tfrac{7}{84}G_d + \tfrac{1}{8}G_1 + 1\tfrac{17}{12}G_3 + \tfrac{1}{48}\Delta_0(s:p) + \tfrac{5}{96}\Delta_0(s:d) + \tfrac{5}{48}\Delta_0(p:d) + \tfrac{5}{12}\Delta_2(p:d)$$

$$A(d^9sp) = F_0(s:p) + 9F_0(s:d) + 9F_0(p:d) + 36A - 56B + 28C - 5G_d - 10G_1 - 35G_3.$$

In an earlier paper,[1] valence-state formulae were given, some of which differ from those here: the previous treatment did not, however, relate to the formation of *hybrid* orbitals (e.g. contrast, in V_4, d^3s, the configuration $s\pi\pi'\delta'$, and the configuration $h_1h_2h_3h_4$, where h_i represents a hybrid d^3s orbital). In addition to the hybrid valence states already described, others of less general interest, but of use to our present purpose, are listed below; several of these relate to paramagnetic valence states, represented by $V_n(m)$, in which only m of the n valence electrons are of indeterminate spin.

Description	Valence-state formula
(i) $V_5(4)$, d^4s; σ^+, $h_1h_2h_3h_4$ ($h_i = d^3s$ hybrid)	$A(d^4s) - 12\frac{3}{4}B + 3\frac{3}{10}C - 2\frac{3}{4}G_2 + \frac{3}{16}\Delta_0$
(ii) $V_5(2)$, d^4s; $s^+\delta^+\delta'^+$, $\pi\pi'$	$A(d^4s) - 13\frac{1}{2}B + 2\frac{1}{2}C - 3G_2$
(iii) $V_4(2)$, d^4s^2; $s^2\delta^+\delta'^+$, $\pi\pi'$	$A(d^4s^2) - 13\frac{1}{2}B + 2\frac{1}{2}C$
(iv) V_0, d^6; $\pi^2\pi'^2\,\delta'^2$	$A(d^6) - 16B + 8C$
(v) $V_3(2)$, d^5s^2; $s^2\delta^2\delta'^2$, $\pi\pi'$	$A(d^5s^2) - 12\frac{1}{2}B + 7\frac{1}{2}C$
(vi) V_2, d^7; $\sigma^2\delta^2\delta'^2$, $\pi\pi'$	$A(d^7) - 3\frac{1}{2}B + \frac{1}{2}C$
(vii) V_2, d^6s^2; $s^2\delta^2\delta'^2$, $\pi\pi'$	$A(d^6s^2) + 6\frac{1}{2}B + 5\frac{1}{2}C$
(viii) V_0, d^8; $\pi^2\pi'^2\delta^2\delta'^2$	$A(d^8) + 4B + 3C$
(ix) $V_3(2)$, d^7s^2; $s^2\delta^2\delta'^2\sigma^+$, $\pi\pi'$	$A(d^7s^2) - \frac{1}{2}B + \frac{3}{4}C$
(x) V_1, d^7; $\pi'^2\delta^2\delta'^2\sigma$	$A(d^7) + 2B + 4C$
(xi) V_2, d^6; $\pi'^2\delta'^2(\sqrt{\frac{2}{3}}\pi - \sqrt{\frac{1}{3}}\delta)\sigma$	$A(d^6) - 11B + 5\frac{1}{2}C$

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(xii) V_3, d^5; $\pi^2\sigma\delta\delta'$	$A(d^5) - 15B + 7\frac{1}{2}C$
(xiii) V_1, d^8s; $\sigma^2\pi^2\pi_1{}^2h_1{}^2h_2$ ($h_i = d^2s$ hybrid)	$A(d^8s) + 4\frac{8}{9}B + 1\frac{31}{45}C - \frac{2}{9}G_2 + \frac{2}{9}\Delta_0$
(xiv) V_2, d^7s; $\sigma^2\delta^2h_1{}^2h_2h_3$ ($h_i = d^3s$ hybrid)	$A(d^7s) - 5\frac{7}{8}B + 3\frac{1}{10}C - 1\frac{1}{8}G_2 + \frac{7}{32}\Delta_0$
(xv) V_3, d^6s; $\pi^2\pi'^2h_1h_2h_3$ ($h_i = d^2s$ hybrid)	$A(d^6s) - 15\frac{1}{3}B + 5\frac{23}{30}C - 2\frac{2}{3}G_2 + \frac{1}{6}\Delta_0$
(xvi) V_4, d^5s; $\sigma^2h_1h_2h_3h_4$ ($h_i = d^3s$ hybrid)	$A(d^5s) - 11\frac{3}{4}B + 7\frac{4}{5}C - 3\frac{1}{4}G_2 + \frac{3}{16}\Delta_0$
(xvii) $V_4(1)$, d^3s; $s^+\delta^+\delta'^+$, π	$A(d^3s) - 3B + C - 2\frac{1}{2}G_2$
(xviii) $V_3(1)$, d^3s^2; $s^2\delta^+\delta'^+\pi$	$A(d^3s^2) - 3B + C$
(xix) V_1, d^5s^2; $s^2\delta^2\delta'^2\pi$	$A(d^5s^2) + 10B + 10C$
(xx) $V_2(1)$, d^6s^2; $s^2\delta^2\delta'^2\sigma^+\pi$	$A(d^6s^2) + 1\frac{1}{2}B + 5\frac{1}{2}C$
(xxi) V_1, d^7s^2; $s^2\delta^2\delta'^2\sigma^2\pi$	$A(d^7s^2) + 5C$

Values are given in the following tables of the energies of excitation required to reach some of the valence states belonging to the elements under consideration. Most of these energy values are calculated from the appropriate valence-state formulae using parameter values listed in Tables 1–6. Others are estimates, based on the average height of terms belonging to the particular configuration in the atomic spectrum; these latter are bracketed in the tables, and should be accepted as approximate values only.

TABLE 7.—ENERGIES (IN eV) OF VALENCE STATES IN V(I), Cr(II), Mn(III)

	V(I)	Cr(II)	Mn(III)
V_5, d_5; C_{5v};	4·82	2·64	3·50
V_5, d^4s; C_{4v};	1·91	3·65	~ 9·6
V_5, d^4p;	(6)	(9)	(17)
V_5, d^3sp;	(5)	—	—
$V_5(4)$, d^4s; T_d;	2·39	4·24	~10·4
$V_5(2)$, d^4s;	1·61	3·48	9·91
V_2, d^3s^2; D_{3h};	1·12	6·62	—

Notes

(i) The parameter values for A, B, C, G_2 for V(I) and Cr(II) are from columns III of Table 1.

(ii) MOORE[4] lists forty-three terms from d^3sp in the V(I) spectrum. The mean position of these is 4·5 eV above ground-level. Allowing for unlocated terms (most of which probably lie above the ionization limit), we estimate that the mean position of all d^3sp lies not less than 5 eV above ground-level. Thirty terms have been located from d^4p in V(I), the mean position of these lying 4·6 eV above ground-level. Allowing for the numerous missing terms, we estimate that the mean position of all d^4p terms is not less than 6 eV above ground-level.

(iii) MOORE[4] lists fifty-one terms from d^4p in Cr(II), mean position 8·8 eV above ground-level. No terms from d^3sp have been located.

(iv) Only six terms from d^4p have been located in Mn(III); these have mean position 14·3 eV, whereas the corresponding terms in Cr(II) lie 6·3 eV above ground-level. Hence, we have placed V_5, d^4p in Mn(III) higher by 8 eV than V_5 in Cr(II).

(v) The values for Mn(III), V_5, d^4s, C_{4v}, and T_d, are calculated neglecting the term in Δ_0, and are probably low on this account. The particular case, $\sin\alpha = \frac{1}{\sqrt{5}}$, is taken for d^4s bonds.

TABLE 8.—ENERGIES (eV) OF VALENCE STATES IN Cr(I), Mn(II), Fe(III)

	Cr(I)	Mn(II)	Fe(III)
V_6, d^5s;	3·33	4·67	~8·5
V_6, d^5p;	(9)	(11)	(17)
V_6, d^4sp;	(7)	(17)	—
V_4, d^6; C_{4v}	5·94	3·64	2·34
V_4, d^4s^2; C_{4v}	2·92	8·98	—
$V_4(2), d^4s^2$;	2·76	8·78	—
V_0, d^6;	7·33	5·20	4·36

Notes

(i) The valence-state energies of Cr(I) are based on the parameters obtained by fitting d^4s^2 and d^5s as a set (Table 2).

(ii) The energy value for Fe(III), V_6, d^5s is calculated neglecting the term in Δ_0, and is probably *c.* ½ eV low on this account.

(iii) Fifty-three terms from d^4sp of Cr(I) are listed by MOORE,[4] mean position 5·9 eV above ground-level. The number of unlocated terms is large (altogether d^4sp should give ninety-eight terms). so that it is difficult to estimate the mean position of the totality of d^4sp terms. Only four terms from d^4sp have been located in the Mn(II) spectrum. These lie some 7–10 eV higher (relative to ground-states) than corresponding terms in Cr(I). No terms from d^4sp have been observed in Fe(III).

(iv) Seventy-five of the seventy-six terms belonging to d^5p have been located in the Fe(III) spectrum, average height 17 eV above ground-level. Forty-five terms from d^5p in Cr(I) (average height 6·5 eV), and twenty terms from d^5p in Mn(II) (average height 8·3 eV) have been located.

TABLE 9.—ENERGIES (eV) OF VALENCE STATES IN Mn(I), Fe(II), Co(III)

	Mn(I)	Fe(II)	Co(III)
V_7, d^5sp;	(8)	(12)	—
V_7, d^5p^2;	(13)	—	—
V_5, d^5s^2; C_{5v}	3·21	6·74	—
V_5, d^6s; C_{4v}	4·05	2·63	~8·1
V_5, d^6p;	(9)	(8·5)	(17)
V_2, d^7; D_{2h}	6·53	1·49	1·70
$V_2(2), d^5s^2$;	5·06	8·95	—

Notes

(i) Twenty-two terms from d^5sp, Mn(I), are listed, average height 6·1 eV above ground-level. Some thirty terms belonging to this configuration remain to be located. We estimate that V_7 lies between 7 eV and 12 eV, and have chosen 8 eV as the "best" estimate. Only eight terms from d^5sp in Fe(II) are known, average height 9·9 eV above ground-level. Since ^6P in Fe(II) lies *c.* 4 eV higher, relative to ^6P in Mn(I), we consider V_7 in Fe(II) to lie at least 4 eV up on V_7 in Mn(I). No terms from d^5sp are known in Co(III).

(ii) One term only, ^6P, from d^5p^2 in Mn(I) has been located. This lies 7·1 eV above ground-level and is *c.* 5 eV higher than ^6P, d^5sp.

(iii) Fifty-one terms from d^6p in Fe(II) are listed by MOORE,[4] mean position 8·5eV above ground-level. Eighteen terms from d^6p in Mn(I) are listed, mean position 6·8 eV above ground-level The mean position of the three sextuplet terms belonging to d^6p is at 5·1 eV in Fe(II), and at 5·4 eV in Mn (I). In Co(III), thirty three terms from d^6p are listed, mean position 15·9 eV. The average height of the sextuplets is 12·7 eV.

(iv) The value for Co(III), V_5, d^6s, is calculated neglecting the term in Δ_0.

TABLE 10.—ENERGIES (eV) OF VALENCE STATES IN Fe(I), Co(II), Ni(III)

	Fe(I)	Co(II)	Ni(III)
V_6, d^6sp;	(7)	(11·5)	—
V_6, d^5s^2p;	(9)	—	—
V_4, d^6s^2; C_{4v}:	2·26	7·53	—
V_4, d^7s; T_d:	2·70	2·86	~8·9
V_4, d^7p;	(6·5)	(8)	(17)
V_2, d^8; C_{2v}:	5·04	1·05	1·34
V_4, d^8; $d^6\pi\pi'$:	4·79	0·79	1·01
V_4, d^6s^2; $s^2d^4\pi\pi'$	5·34	11·25	—
V_0, d^8;	6·62	2·75	3·48

Notes

(i) Thirty-seven of the sixty-six terms predicted for d^6sp have been located in the Fe(I) spectrum. The mean position of the known terms lies 5·2 eV above ground-level. Allowing for missing terms, we estimate 7 eV for V_6, d^6sp. Only three terms belonging to d^6sp are known in Co(II); these lie higher than their counterparts in Fe(I) by *c.* 4½ eV. No terms from d^6sp are known in Ni(III).

(ii) Two terms from d^5s^2p are known in Fe(I); the lowest term, ^7P, lies 5 eV above ground-level. The lowest term, ^7D, of d^6sp lies *c.* 2·5 eV above ground-level, so that V_6, d^5s^2p is probably 2 or 3 eV higher than V_6, d^6sp.

(iii) Thirty-three terms from d^7p of Fe(I) are listed, mean position 5·9 eV above ground-level. Allowing for missing terms, V_4, d^7p is estimated at 6·5 eV. In Co(II) (and similarly in Ni(III)), only eleven terms have been identified from d^7p. All six sextuplet terms are known in Fe(I), Co(II), and in Ni(III); the mean position of the sextuplets in Fe(I) is 5 eV above ground-level, in Co(II) 6·6 eV above ground-level, and in Ni(III) 15 eV above ground-level.

(iv) The value for Ni(III), V_4, d^7s, is calculated neglecting the term in Δ_6.

TABLE 11.—ENERGIES (eV) OF VALENCE STATES IN Co(I), Ni(II), Cu(III)

	Co(I)	Ni(II)	Cu(III)
V_5, d^7sp;	(7)	—	—
V_2, d^7s^2; D_{2h}:	1·65	—	—
V_2, d^8s; D_{2h}:	2·84	~3·25	~10·14
V_2, d^8p; C_{2v}:	—	~7·97	—
$V_3(2), d^7s^2$;	2·39	—	—
V_1, d^9;	3·46	0·07	1·10

Notes

(i) Thirty-two terms from d^7sp are known in Co(I), average height 5·1 eV above ground-level. Allowing for the numerous missing terms, we place V_5, d^7sp at *c.* 7 eV. No terms from d^7sp are known in Ni(II) and Cu(III).

(ii) The values for V_2, d^8s, of Ni(II) and Cu(III) are calculated neglecting the term in Δ_6, and the value for V_2, d^8p of Ni(II) neglects the terms in $F_2(p:p)$ and Δ_6.

TABLE 12.—ENERGIES (eV) OF VALENCE STATES IN Ni(I), Cu(II), Zn(III)

	Ni(I)	Cu(II)	Zn(III)
V_4, d^8sp;	(6)	(17)	(35)
V_3, d^8s^2; C_{2v}:	1·23	10·11	—
V_3, d^8s^2; $d^8s^2\pi\pi'$:	0·91	9·73	—
V_2, d^9s; C_{2v}	0·65	3·59	(>10)
V_2, d^9p; D_{2h}:	~3·72	~8·54	~17·5
V_0, d^{10};	1·82	0·0	0·0
V_0, d^8s^2;	3·18	12·33	—

Notes

(i) Terms from d^8p^2 have not been located in these spectra, so that we have been unable to apply the valence-state formula for V_2, d^9p in full: the quoted values for d^9p are obtained by neglecting the terms in Δ_6 and Δ_3.

(ii) Twenty-one terms from d^8sp have been located in Ni(I), average height 4·9 eV above ground-level. Allowing for the seventeen missing terms, we place V_4 *c.* 6 eV above ground-level. Twenty-nine terms from d^8sp are listed in Cu(II), mean position 16 eV above ground-level. Twelve terms from d^8sp are known in Zn(III).

TABLE 13.—ENERGIES (eV) OF VALENCE STATES IN Cu(I)

V_2, d^9sp; C_{2v}:	~5·5
$V_1, d^{10}s$;	0·00
V_1, d^9p;	3·81
V_1, d^9s^2;	1·49

Notes

(i) RACAH[14] gives the following parameter values in Cu(I), d^9sp, $F_2(p:d) = 315·5$; $G_p = 6906$; $G_d = 901$; $G_1 = 391·5$; $G_3 = 95$. The term values given by MOORE[4] require $A(d^9sp) = 48833$

(ii) The value calculated for V_2, d^9sp, neglects several terms which we have been unable to estimate, and is probably low for this reason.

3. ELECTRONEGATIVITIES AND VALENCE-STATE IONIZATION POTENTIALS

The electronegativity of an atom in a given valence state may be related, according to MULLIKEN,[15] to the sum of the valence-state ionization potential and electron affinity of the atom. The method cannot be fully applied to most of the elements considered here, since electron affinity values are unknown. In the case of Cu and Ni, however, one can evaluate the electron affinities by GLOCKLER's[16] extrapolation method.

(a) *Copper*

PRITCHARD and SKINNER[17] obtained 0·9 eV for the electron affinity of Cu by GLOCKLER's method, and derived $x_p = 1·36$ for the *s*-electronegativity on the Pauling

[14] G. RACAH *Phys. Rev.* **62**, 523 (1942).
[15] R. S. MULLIKEN *J. chem. Phys.* **2**, 782 (1934).
[16] G. GLOCKLER *Phys. Rev.* **46**, 111 (1934).
[17] H. O. PRITCHARD and H. A. SKINNER *Chem. Rev.* **55**, 745 (1955).

scale. The thermochemical estimate by HAISSINSKY[18] of the electronegativity of univalent Cu is appreciably higher (1·8). Using the excitation energies given in Tables 12 and 13, we may derive

$$\text{(i) } Cu^- (d^{10}s^2, V_0) \rightarrow Cu(d^9s^2, V_1) : E = 2{\cdot}39 \text{ eV}.$$

$$\text{(ii) } Cu (d^9s^2, V_1) \rightarrow Cu^+(d^8s^2, V_0) : I = 18{\cdot}56 \text{ eV}.$$

whence $\frac{1}{2}(I + E) = 10{\cdot}48$ eV, and $x_p = \dfrac{I + E}{6{\cdot}3} = 3{\cdot}32$.

The state V_1, d^9s^2, is thus much more electronegative than the state V_1, $d^{10}s$. An explanation of the thermochemical electronegativity value might be given in terms of the usage by univalent Cu in its compounds of isovalent[19] *ds* hybrids possessing *c.* 23% *d*-character.

It is possible to make a *rough* estimate of the electronegativity of the trivalent state, V_3, d^9sp. The *d*-electronegativity of this state is high, thus:

$$\text{(iii) } Cu^- (d^{10}sp, V_2) \rightarrow Cu(d^9sp, V_3) : E \sim 4{\cdot}3 \text{ eV}.$$

$$\text{(iv) } Cu(d^9sp, V_3) \rightarrow Cu^+(d^8sp, V_2) : I \sim 20 \text{ eV}.$$

Assuming that the *s*- and *p*-electronegativities are determined primarily by the ionization potential terms, viz.

$$\text{(v) } Cu(d^9sp, V_3) \rightarrow Cu^+(d^9p, V_2) : I \sim 10{\cdot}7 \text{ eV}.$$

$$\text{(vi) } Cu (d^9sp, V_3) \rightarrow Cu^+(d^9s, V_2) : I \sim 5{\cdot}6 \text{ eV}.$$

we obtain $x_p = 2{\cdot}14$ for the electronegativity of the *dsp* hybrid orbitals of d^9sp, V_3. HAISSINSKY,[18] using the thermochemical method, obtained $x_p = 2{\cdot}0$ for Cu in the divalent state.

(b) *Nickel*

Extrapolation through the ionization potentials $M(d^{10}s) \rightarrow M^+(d^{10})$ in the isoelectronic series M = Cu, Zn^+, Ga^{2+}, gives $Ni^-(d^{10}s) \rightarrow Ni(d^{10}) : E = -0{\cdot}01$ eV. Extrapolation through the appropriate term values in Cu, Zn^+, (Ga^{2+}), and Ge^{3+} indicates that $Ni^-(d^9s^2)$ is more stable than $Ni^-(d^{10}s)$ by 1·03 eV. The ionization potential of Ni is given as 7·63 eV by MOORE.[4] Hence,

$$Ni^-, d^{10}s, V_1 \xrightarrow[E = -1{\cdot}18]{} Ni, d^9s, V_2 \xrightarrow[I \sim 11{\cdot}93]{} Ni^+, d^8s, V_1$$

$$Ni^-, d^9s^2, V_1 \xrightarrow[E = -0{\cdot}15]{} Ni, d^9s, V_2 \xrightarrow[I = 7{\cdot}05]{} Ni^+, d^9, V_1$$

leading to 1·71 for the *d*-electronegativity,* 1·095 for the *s*-electronegativity, and ~1·40 for the *ds*-hybrid electronegativity in Ni, d^9s, V_2. The electronegativity in the state d^8s^2, V_2, is markedly higher than in d^9s, V_2. Although terms from d^7s^2 have not

* We have estimated $A(d^7s^2)$ of Ni(II) ~ 67,200 cm^{-1}, from the probable position of Ni on curve *C* of Fig. 1.

[18] M. HAISSINSKY *J. Phys.* **7**, 7 (1946).

[19] R. S. MULLIKEN *J. phys. Chem.* **56**, 295 (1952).

been located in the spectrum of Ni(II), the valence-state excitation energy can be estimated from curve *C* of Fig. 1; hence, we obtain

$$Ni^-(d^9s^2, V_1) \xrightarrow[E=0{\cdot}43]{} Ni(d^8s^2, V_2) \xrightarrow[I\sim 17]{} Ni^+(d^7s^2, V_1)$$

leading to $x_p \sim 2{\cdot}8$. The thermochemical estimate of the electronegativity of divalent Ni by HAISSINSKY is 1·7.

For the remaining elements we have calculated some of the important valence-state ionization potentials, which are presented graphically in Fig. 1.

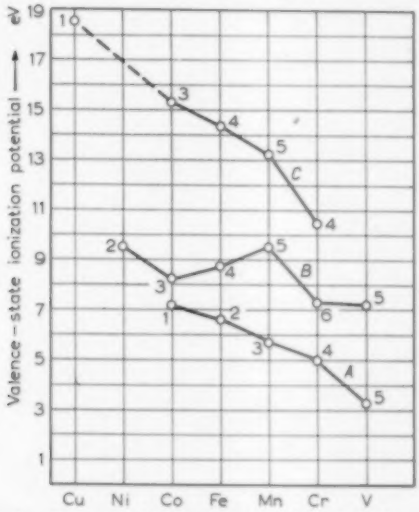


FIG. 1.—Curve *A* : *d* ionization potentials of d^n, V_m
B : *d*-*s*-hybrid ionization potentials of $d^{n-1}s, V_m$
C : *d* ionization potentials of $d^{n-2}s^2, V_m$
The numbers adjacent to each point shown on the curves give the values of *m* in V_m.

In Fig. 1. curve *A* gives the *d*-ionization potentials of M, d^n, (M = Co, Fe, Mn, Cr, and V), curve *B* gives the ionization potentials of the hybrid orbitals of M, $d^{n-1}s$, (M = Ni, Co, Fe, Mn, Cr, and V), and curve *C* gives the *d*-ionization potentials of M, $d^{n-2}s^2$ (M = Cu, Ni, Co, Fe, Mn, Cr, and V). One feature of interest in Fig. 1 is that a valence-state ionization potential is generally higher in a state $d^{n-2}s^2$ than in $d^{n-1}s$, and is least in d^n. There is little doubt that the valence-state electron affinities are smallest (and probably negative) in d^n, and are largest in $d^{n-2}s^2$: thus the separations between the ionization potential curves will increase on plotting $(I + E)$. Thus, it appears that the electronegativity increases in passing from states $d^n \rightarrow d^{n-1}s \rightarrow d^{n-2}s^2$ of a given element of the group.

4. STABILITY OF THE HIGHER COVALENCIES

The elements in the period from V to Cu are reluctant to form compounds (other than co-ordination complexes) in which the metals show both high covalency and high co-ordination number (C.N.). Thus, vanadium pentafluoride is the only known pentahalide of vanadium. The tetrachloride, VCl_4, which is paramagnetic, shows no particular tendency to dimerize[20] to V_2Cl_8. No hexahalide of chromium had been

[20] A. G. WHITTAKER and D. M. YOST *J. chem. Phys.* **17**, 188 (1949).

prepared, although the complex ion CrF_6^{3-} is well known. The highest fluoride of neutral chromium is the pentafluoride,* reported by VAN WARTENBERG,[22] and the highest chloride so far prepared is the unstable $CrCl_4$. Manganese may be considered to show its maximum covalency of 7 in the unstable compounds MnO_3F and Mn_2O_7, in which, however, it is noteworthy that the C.N. is only 4. The trifluoride, MnF_3, is the highest that has been prepared. SIDGWICK[23] considers that there is satisfactory evidence for the existence of $MnCl_4$ in solution. From Fe and Co, the trifluorides are the highest that have been prepared, and from Ni, the difluoride.

On the other hand, each of these elements forms complex cations in which the metal ion is octahedrally 6-co-ordinated, and all except Ni and Cu form complex anions with C.N. = 6. Moreover, high C.N.s are achieved in the neutral co-ordination compounds of these elements. Thus, in the metal carbonyls, C.N.s ranging from 4 to 7 occur,[24–27] viz:

$Cr(CO)_6$	$Mn_2(CO)_{10}$	$Fe(CO)_5$	$Fe_2(CO)_9$	$Fe_3(CO)_{12}$	$Co_2(CO)_8$	$Ni(CO)_4$
6	6	5	7	6,4	6	4

The instability of the higher covalencies in the compounds of these elements does not necessarily imply an *absolute* thermodynamic instability, but reflects a *relative* instability with respect to the lower valency compounds. We might illustrate this point from the chromium chlorides, of which only $CrCl_2$, $CrCl_3$, and $CrCl_4$ have been prepared. The heats of formation ($-\Delta Hf°$) are given[28] as 94·6 for $CrCl_2$ (cryst), 134·6 for $CrCl_3$ (cryst), and 104 kcal/mole for $CrCl_4$ (gas). The mean bond dissociation energies $\bar{D}$(Cr–Cl), may be calculated (using heats of sublimation given by KUBACHEWSKI and EVANS[29]) and are 85, 80, and 75 kcal/mole respectively in gaseous $CrCl_2$, $CrCl_3$, and $CrCl_4$ molecules. Unless, therefore, there occurs an unusually sharp discontinuity at $CrCl_5$, this compound cannot be an endothermic substance. Extrapolation through the $\bar{D}$(Cr–Cl) values gives 70 kcal/mole in $CrCl_5$, leading to $-\Delta Hf° \sim 124$ kcal/mole for gaseous $CrCl_5$. Nevertheless, gaseous $CrCl_5$ (as is $CrCl_4$) would be endothermic with respect to crystalline $CrCl_3$.

In the case of the highest covalencies of 8 and 9 which would derive from the valence states d^4sp^3, V_8 of Fe, and d^5sp^3, V_9 of Co, the very high excitation energies required to attain them probably debar their use. It is of interest to enquire if this factor applies more generally. For example, although d^4s, V_5 is the lowest lying of the pentavalent states of vanadium, we consider d^3sp, V_5, to be the parent configuration in vanadium compounds with C.N. = 5. The structure of VF_5 has not been determined, but analogy with the pentahalides of niobium[30] points to the trigonal bipyramid

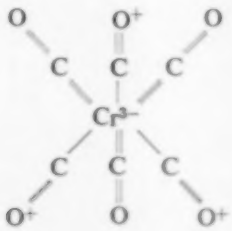
* FOWLER, ANDERSON *et al.*[21] state that there is evidence of gaseous CrF_4 together with lower fluorides formed on reacting F_2 with $CrCl_3$ or Cr_2O_3. They were unable to confirm the formation of CrF_6.

[21] R. D. FOWLER, H. C. ANDERSON, J. M. HAMILTON, *et al.* *Industr. engng. Chem.* **39**, 343 (1947).
[22] H. VAN WARTENBERG *Z. anorg. Chem.* **247**, 135 (1941).
[23] N. V. SIDGWICK *Chemical Elements and Their Compounds* Oxford Univ. Press (1950).
[24] E. D. BRIMM, M. A. LYNCH, and W. J. SESNY *J. Amer. chem. Soc.* **76**, 3831 (1954).
[25] R. K. SHELINE *J. Amer. chem. Soc.* **73**, 1615 (1951).
[26] J. W. CABLE, R. S. NYHOLM, and R. K. SHELINE *J. Amer. chem. Soc.* **76**, 3373 (1954).
[27] H. M. POWELL and R. V. G. EWENS *J. chem. Soc.* 286 (1939).
[28] *Selected Values of Chemical Thermodynamics Properties* Nat. Bur. Stands, Washington, Circular 500 (1952).
[29] O. KUBASCHEWSKI and E. EVANS *Metallurgical Thermochemistry* Butterworth-Springer, London (1951).
[30] H. A. SKINNER and L. E. SUTTON *Trans. Faraday Soc.* **36**, 668 (1940).

arrangement, and thus to d^3sp hybridization.* The preference for d^3sp is presumably due to the higher bond-forming power† of d^3sp hybrid orbitals relative to d^4s orbitals. It is also possible that d^4s, V_5 is too electropositive to support five covalent bonds. (The valence-state ionization potentials suggest that d^3sp is appreciably more electronegative than d^4s.) On the other hand, d^4s may be favoured in the V_5 valencies associated with C.N.s of 4, 3, or 2. The tetrahedral arrangement[31] in VCl_4, which points to d^3s hybridization, is not inconsistent with d^4s, $V_5(4)$, as parent.

The instability of hexacovalent Cr can hardly be ascribed to the difficulty of reaching a V_6 state, since d^5s, V_6 lies at a very moderate height above ground-level. But d^5s is an unsuitable parent of C.N. = 6, due to incompatibility in the *d*- and *s*-orbitals towards hybridization[32], and possibly because the state is too electropositive. The state d^4sp, V_6, is probably superior to d^5s in these respects, and it could be the parent from which CrF_5 is formed (by partial hybridization to give d^3sp hybrid orbitals). The instability of CrF_6 suggests that total hybridization to produce six d^4sp prismatic orbitals does not give orbitals of sufficient bonding power. The strongest type of hexacovalent orbitals are believed to be the octahedral d^2sp^3 hybrids,[33] but d^2sp^3, V_6 in neutral Cr is clearly difficult to reach since d^4sp already lies 7 eV above ground-level, and the further promotions $d^4sp \rightarrow d^3sp^2 \rightarrow d^2sp^3$ must require considerable additional energy expenditure. However, the difficulty of attainment of d^2sp^3 is not a sufficient reason for instability in CrX_6. Consideration must also be given to the donor propensity of the adducts X. Hence, the instability of CrF_6 could ultimately be ascribed to the inability of F to back-co-ordinate strongly enough to support the structure

and thus neutralize the high promotional energy. Conversely the stability of $Cr(CO)_6$ is due to the willingness of CO to display donor behaviour, giving weight to structures of the type



Hexavalent Cr more readily forms covalent compounds of C.N. = 4, in which

* Or possibly to dsp^3 hybridization. The relative merits of these two valence states may be discussed in a later paper.

† Jaffé and Doak[20] state that the overlap power of $d^n s$ orbitals is less than that of $d^{n-1}sp$ orbitals, and that replacement of *d* by *p* usually increases overlap power.

[31] W. N. Lipscomb and A. G. Whittaker *J. Amer. chem. Soc.* **67**, 2019 (1945).

[32] G. Kimball *J. chem. Phys.* **8**, 188 (1940).

[33] G. H. Duffey *J. chem. Phys.* **17**, 1328 (1949).

the tetrahedral arrangement is adopted (e.g. CrO_2Cl_2,[34] chromic oxide.[35]) The relative stability of these compounds may be in part due to the stability of the low-lying V_6 states (d^5s, d^4sp) towards the formation of four σ-orbitals (d^3s or d^2sp hybrids) leaving π-orbitals available for multiple bonding. PAULING,[36] in a discussion on the stability of the oxyacids of these elements, concludes that the π-bonding of the metal atoms is primarily responsible for the stability of C.N. = 4. The molecular orbital treatment of WOLFSBERG and HELMHOLTZ[37] on the ions MnO_4^- and $CrO_4^=$ supports this view, their calculations showing these π-bonds to be exceptionally strong.

The instability of the alkyls of the transition metals has been discussed in terms of molecular orbital theory by JAFFÉ and DOAK,[38] who found that the overlap integrals between d^ns hybrid orbitals of these metals and sp^3 carbon orbitals are relatively small by comparison with, e.g., the overlap integral between Zn sp-hybrid and C sp^3-orbitals. We would suggest that the instability of metal alkyls reflects the instability of the higher C.N.s (and higher valencies) in these elements. Each of the following factors may be quoted against the formation of stable alkyl derivatives:

(i) The alkyl groups are insufficiently electronegative to give essentially ionic compounds deriving from the metal ions,
(ii) Covalent alkyls deriving from the higher valency states of the metal cannot be stabilized by adopting a low C.N. (4 or less), since the alkyl groups are unable to form π-bonds to the metal,
(iii) Covalent alkyls deriving from the lowest lying of the higher valency states of the metal would have weak metal-carbon bonds due to the relatively weak bond-forming power in the valence states d^ns (JAFFÉ and DOAK),
(iv) The lack of donor power by alkyl groups does not assist the attaining of the most suitable higher valence states of the metal.

In the *cyclo*pentadienyl derivatives of these metals, as PAUSON[39] points out, the situation is quite different, in terms of overlapping of the orbitals, from that in the alkyl derivatives.

5. THE METAL DI*CYCLO*PENTADIENYLS

The metal di*cyclo*pentadienyls of the elements from V to Ni are, with the single exception of the Mn derivatives,[40] covalent compounds. The compounds are unique in this respect, other MX_2 compounds of these elements being essentially ionic in character. The unusual metal-carbon bonding in the metal di*cyclo*pentadienyls has been discussed in detail by MOFFITT.[41] Our concern is with the electronegativity of the d_π orbitals of the metal engaged in "sandwich" bonding.

The valence states employed by the metals in these compounds must be chosen to comply with the known magnetic properties of the substances, and, if MOFFITT's formulation of the "sandwich" bonding is accepted, have the d_π and $d_{\pi'}$ orbitals singly occupied, and the d_σ orbital, preferably, vacant. Suitable valency states in the case of V, Cr, and Fe are therefore $V_5(2)$, $s^+\delta^+\delta'^+$, $\pi\pi'$, $V_4(2)$, $s^2\delta^+\delta'^+$, $\pi\pi'$, and

[34] K. J. PALMER *J. Amer. chem. Soc.* **60**, 2360 (1938).
[35] A. BYSTRÖM and K.-A. WILHELMI *Acta. chem. scand.* **4**, 1131 (1950).
[36] L. PAULING *Victor Henri Commemorative Volume* Desoer, Leige (1948).
[37] M. WOLFSBERG and L. HELMHOLTZ *J. chem. Phys.* **20**, 837 (1952).
[38] H. H. JAFFÉ and G. O. DOAK *J. chem. Phys.* **21**, 196 (1953).
[39] P. L. PAUSON *Quart. Rev.* **9**, 391 (1955).
[40] G. WILKINSON and J. M. BIRMINGHAM *J. Amer. chem. Soc.* **76**, 6210 (1954).
[41] W. MOFFITT *J. Amer. chem. Soc.* **76**, 3386 (1945).

V_2, $s^2\delta^2\delta'\ \pi\pi'$, respectively, for which the d_π ionization potentials are 7·1 eV, 10·9 eV, and 15·1 eV. We do not know the d_π electron affinities, but they are almost certainly small by comparison with the ionization potentials. Hence the electronegativities, x_p, are approximately 1·1 in V, 1·8 in Cr, and 2·4 in Fe. The values for Cr and Fe are consistent with essentially covalent metal-to-carbon bonding, but the calculated vanadium electronegativity is difficult to reconcile with covalent bonding. An alternative valence-state $V_3(2)$, $s^2\delta^+,\ \pi\pi'$ is much more electronegative, but would not account for the observed paramagnetic moment in the di*cyclo*pentadienyl derivative.[62]

The valence-states $V_3(2)$, $s^2\delta^2\delta'^2\sigma^+,\ \pi\pi'$ in Co, and V_2, $s^2\delta^2\delta'^2\sigma^2,\ \pi^+\pi'$, in Ni are accepted for present purposes as representing the metal atoms in $Co(C_5H_5)_2$ and $Ni(C_5H_5)_2$. The calculated d_π ionization potentials of these states are, respectively, 16·1 eV and *c.* 17·6 eV, leading to x_p values of 2·5 and 2·8, consistent with covalent bonding.

Acknowledgements—The authors wish to thank Dr. H. O. PRITCHARD for assistance with the computations. We are also much indebted to the referee of this paper, whose valuable comments on the original draft led us to the more detailed treatment here presented.

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SOME IONIZATION POTENTIAL VARIATIONS AND RELATIONSHIPS—II

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Abstract—The paper is in two parts. Variation of the higher (>2) ionization potentials of the 3*d* transition elements (Sc to Zn) is examined in the first part. Ionization potential increases regularly with atomic number except for sharp discontinuities which can be correlated with half-shell completion. It has not been possible to explain satisfactorily either the large magnitude (3–4 volts) of these discontinuities or the fact that variation of ionization potential after a discontinuity appears to be the same as before a discontinuity.

The second part is devoted to a study of possible correlations between ionization potential *differences* and variable valence (number and stability of valence states) in the transition elements. Correlations are as a rule quite distinct and use may be made of ionization potential differences to provide a plausible account for a variety of differences in valence behaviour; for example, differences between Ti and Zr, Hf and Th; between Fe + Co and Ru; and between Mn and Re.

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PREVIOUS papers on ionization potentials by this writer[1–6] considered a variety of topics. One[5] was concerned mainly with ionization potential variation in different elements and along iso-electronic sequences: the present paper continues the study of ionization potential variations and is confined largely to the transition elements. It is divided into two parts.

We examine first the variation of the third and higher ionization potentials in the 3*d* transition series, Sc to Cu, with particular regard to the possible effects of half-shell closure. Discussion on a possible correlation between ionization potential *differences* and the existence of valence states and their stability follows. This is an attempt to gain some clearer insight into such problems as to why valence states II and III are either extremely feeble or completely missing in Zr(d^2s^2), Hf(d^2s^2), and Th (probably d^2s^2), yet present in Ti, also d^2s^2; why "oxidation" in Fe(d^6s^2) and particularly Co(d^7s^2) and Ni(d^8s^2) to higher states is held up, whereas in Ru(d^7s^1), a whole array of valence states (II, III, IV, V, VI, VII, and VIII) are present. There is also the interesting problem of the difference in valence properties between the two group VII elements Mn and Re (both d^5s^2).

Although the higher ionization potentials of most of the transition elements are imperfectly known, the general magnitudes usually appear to serve satisfactorily for revealing those features which are quite distinct. As in the previous communication,[5] ionization potentials are drawn mainly from LANDOLT-BÖRNSTEIN[7] and FINKELNBURG and HUMBACH.[8]

[1] L. H. AHRENS *Geochim. et Cosmochim. Acta* **2**, 155 (1952).
[2] L. H. AHRENS *Nature, Lond.* **169**, 463 (1952).
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[4] L. H. AHRENS *Nature, Lond.* **74**, 644 (1954).
[5] L. H. AHRENS *J. inorg. nucl. Chem.* **2**, 290 (1956).
[6] L. H. AHRENS and D. F. C. MORRIS *Ibid.* **3**, 263; **3**, 270 (1956).
[7] LANDOLT-BÖRNSTEIN *Atom und Molekularphysik*, Atom und Ionen. Vol. 1. p. 211. Springer, Berlin-Göttingen (1950).
[8] W. FINKELNBURG and W. HUMBACH *Naturwissenshaften* **42**, 35 (1955).

PART I. VARIATIONS OF THE HIGHER IONIZATION POTENTIALS IN THE 3*d* TRANSITION ELEMENTS

Variation of the second ionization potential with atomic number has been examined.[5] It was found that I_2 varied quite regularly[5] (Fig. 11) with Z, except for discontinuities at Cr and Cu where I_2 was elevated. Such elevation is expected, because d electrons are involved in Cr (d^5s^1) and Cu ($d^{10}s^1$) and general experience (see various diagrams of AHRENS[5]) has shown that the ionization potential is distinctly elevated when passing from an s to a d electron. Ionization in a transitional element might, however, lead to some rearrangement of outer electrons. Thus, for example, Table 1 compares the states of the neutral atom of the 3*d* transition group with states of the singly ionized atom (all states from BACHER and GOUDSMIT[9]).

TABLE 1.— ELECTRON STATES OF NEUTRAL AND SINGLY IONIZED ATOMS OF MEMBERS OF THE 3*d* TRANSITION SERIES

	Neutral	Singly ionized
Sc	d^1s^2	d^1s^1
Ti	d^2s^2	d^2s^1
V	d^3s^2	d^4
Cr	d^5s^1	d^5
Mn	d^5s^2	d^5s^1
Fe	d^6s^2	d^6s^1
Co	d^7s^2	d^8
Ni	d^8s^2	d^9
Cu	$d^{10}s^1$	d^{10}

If rearrangement takes place as indicated in Table 1, elevation of I_2 would also be expected in V, Co, and Ni (states for V^+, Co^+, and Ni^+, respectively, d^4, d^8, and d^9), but no sign of this was found. Variation of I_2 seems therefore to accord with that anticipated from the state of the neutral atom; in which case, if rearrangement has taken place, the rearranged $s \rightarrow d$ electron appears to be indistinguishable from an s electron.

The problem of $s \rightarrow d$ rearrangement during ionization does not arise when considering ionization potentials greater than two, as d electrons only are involved. Consider first the variation of the third ionization potential. Fig. 1 relates I_3 to atomic number over the range Ca(s^2) to Zn($d^{10}s^2$). For most elements, two ionization potentials have been plotted, one from LANDOLT-BÖRNSTEIN[7] and the other from FINKELNBURG and HUMBACH.[8] The straight lines as shown have been arbitrarily drawn.

The third ionization potential is high (51 volts) in calcium because a large amount of energy is required to remove an electron from the completed M shell. In Sc(d^1s^2), I_3 drops to 24·9 volts, and then increases in each succeeding element up to Mn. The increase of about 3 volts from Sc to Ti is considerably greater than the increase in the succeeding elements, which appears to be fairly uniform at ~2 volts per unit increase of Z. The drop from Mn(d^5s^2) to Fe(d^6s^2) is about 3·5 to 4·0 volts, and the following increase from Fe to Co is about the same. From Co to Zn, increase of

[9] R. F. BACHER and S. GOUDSMIT *Atomic Energy Levels.* McGraw Hill, New York (1932).

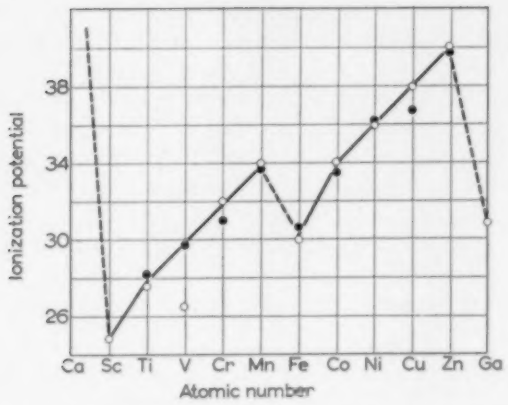

FIG. 1.—Variation of the third ionization potential from Ca to Ga ($Z = 20$ to $Z = 31$). From Ti to Zn, two ionization potentials have been plotted—open circles (LANDOLT-BÖRNSTEIN) and filled circles FINKELNBURG and HUMBACH).

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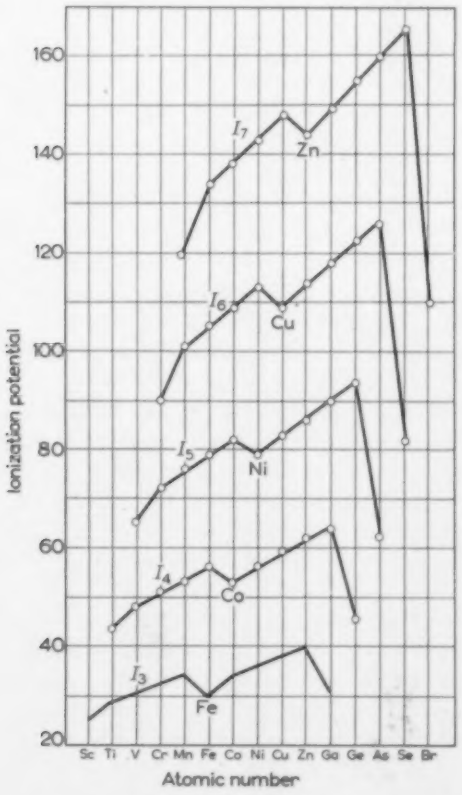

FIG. 2.—Variation of I_2, I_4, I_5, I_6, and I_7 with atomic number. Vertical scale half that of Fig. 1.

I_3 per unit increase of Z appears again to be roughly uniform at ~2 volts. The drop at Ga(s^2p^1) is due to the appearance of a p electron, and I_3 is thus the energy required to remove the single s electron from outside the completed d^{10} shell.

Variations of I_4, I_5, I_6, and I_7 with atomic number are shown in Fig. 2 together with that of I_3 for comparison. The vertical scale is half that of Fig. 1. Ionization potentials are from LANDOLT-BÖRNSTEIN.[7] Variations of I_4, I_5, I_6, and I_7 show the same general features as that of I_3. In general, rate of change of I_n with atomic number increases from I_3 to I_7; the magnitude of the ionization potential drop at each of the successively displaced discontinuities appears, however, to remain roughly uniform at about 3 to 4 volts.

Unlike the apparent uniformity of the ionization potential drop after half-shell completion (see discussion below), the drop after shell closure increases regularly with ionic charge (Fig. 2 and Table 2).

Figs. 1 and 2 may be compared with ionization potential variations involving p electrons (Fig. 3). Here I_1, I_2, I_3, and I_4 are plotted for $3p$ and $4p$ electrons (Al, Si,

TABLE 2.—IONIZATION POTENTIAL DECREASE DUE TO COMPLETION OF d^{10} SHELL

$Zn^{3+} \rightarrow Ga^{3+}$	~9 volts	(i.e. ~1 × 9)
$Ga^{4+} \rightarrow Ge^{4+}$	~18 volts	(i.e. ~2 × 9)
$Ge^{5+} \rightarrow As^{5+}$	~31 volts	(i.e. ~3½ × 9)
$As^{6+} \rightarrow Se^{6+}$	~46 volts	(i.e. ~5 × 9)
$Se^{7+} \rightarrow Br^{7+}$	~62 volts	(i.e. ~7 × 9)
$Br^{8+} \rightarrow Kr^{8+}$	~83 volts	(i.e. ~9 × 9?)
$Kr^{9+} \rightarrow Rb^{9+}$	~104 volts	(i.e. ~11½ × 9)
$Rb^{10+} \rightarrow Sr^{10+}$	~126 volts	(i.e. ~14 × 9)

P . . . ; Ga, Ge, As . . . ; etc.). The discontinuities at P→S and As→Se (first ionization potential) are well known. The magnitudes of these discontinuities are much smaller than those associated with the $3d$ discontinuity at Mn→Fe. In general, the relationships of the $3p$ electrons remain the same, except for increase in slope with increase in ionization potential, and in this respect are similar to the relationships in Fig 2; the $4p$ relationships, however, tend to alter as higher ionization potentials become involved and the sharp discontinuity due to half-group completion disappears (see for example the I_4 relationship in Fig 3). Separation between the $2p$ and $3p$ relationships increases with increase in ionic charge.

In attempting to interpret the main features of Figs. 1, 2, and 3, we may refer briefly to a commonly used description of the electron distribution as a basis for discussion. According to HUND's multiplicity rule, electrons would enter separate orbitals singly when going from Sc to Mn. A half-group or shell of five such single unpaired electrons is complete at Mn. Subsequent electrons (Fe to Zn) with opposing spins pair off with those already present to give a complete shell of ten electrons made up of five doubly occupied orbitals.

The discontinuity at Mn → Fe may be clearly correlated with the completion of the half-group of five $3d$ electrons. The magnitude (~3·5 volts) of the decrease may be compared with that of ~9 volts at Zn → Ga due to filling of the second half-group and hence completion of the whole group of ten $3d$ electrons. At the Zn → Ga

discontinuity, I_3 refers of course to distinctly different electrons, namely $3d$ and $4s$ respectively. (When passing from Ca to Sc, I_3 drops by 26 volts.)

The displaced discontinuities of Fig. 2 may also be correlated with half-shell completion. Consider, for example, variation of I_4. When iron (d^6s^2) is reached, removal of three electrons will have left five $3d$ electrons, and I_4 is therefore the energy required to remove one of these "half-shell" electrons; in Co(d^7s^2) removal of three electrons would leave six $3d$ electrons arranged presumably into a stable half-shell of

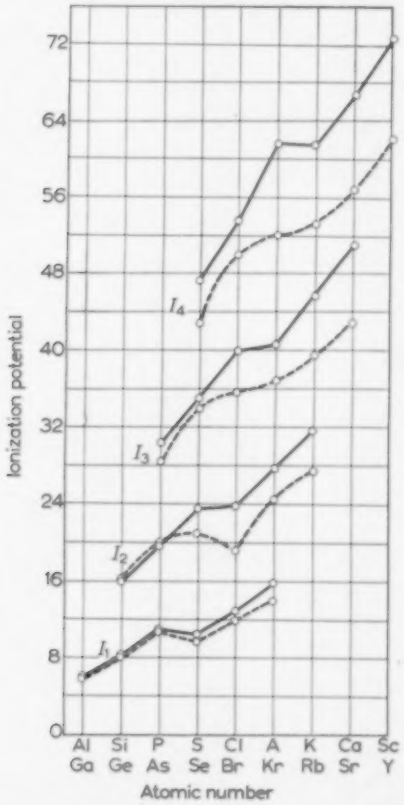

FIG. 3.—Variation of I_1, I_2, I_3, and I_4 for $3p$ and $4p$ electrons. Compare half-shell effects with Fig. 2.

five plus a single electron, and I_4 is the energy required to remove this "lone" electron. In the same way, I_5, I_6, and I_7 refer respectively to the energies required to remove the "lone" electrons in Ni, Cu, and Zn, thus leading to the successive displacements in Fig. 2.

Although there is a clear correlation between half-shell completion and the discontinuities of Figs. 1 and 2, difficulties arise when attempting a fuller interpretation of some of the features of these diagrams in terms of the above description of electron distribution.

There are several factors which might be expected to be the actual cause of discontinuities at this point; for example, (i) inter-electronic repulsion, (ii) the slightly

different energy levels corresponding to different spin orientations, and (iii) change of symmetry. None of these seem adequate to explain the magnitude of the observed discontinuities, and it might be expected further that (i) would cause the slope between Fe and Zn to be less than that between Sc and Mn, whereas it appears to be the same.

PART 2. VARIABLE VALENCE IN THE TRANSITION ELEMENTS

Introduction

The previous paper on ionization potential variations[5] included a brief general study on ionization potential differences and the existence of shells, sub-shells, and valence states in general. Correlations were in general quite distinct, provided some allowance was made for weight and/or size of atom. The emphasis in the present paper is on the transition elements.

When attempting to seek some general correlation between ionization potential differences and the existence and stability of valence states, some difficulties may arise as a result of (i) an inability to satisfactorily define "stability of a valence state," and (ii) variation of bond type. In a rather general way the stability of a valence state is often determined by its tendency either to reduce to lower or oxidize to higher valence states. Thus, Mn^{II} may be described as quite stable, but Ti^{II} would be described as feebly stable because of its tendency to oxidize to higher states. This tendency is much higher in Zr (same general electronic configuration as Ti) and the stability of Zr^{II} is so feeble that its existence is in doubt.

Other factors (crystal-field theory, for example) should be considered in a general discussion on the stabilities of valence states, but for the rather restricted purpose of seeking correlations, as outlined above, this will not be attempted.

A large number of bond types are involved when considering the valence states of a variety of elements, and this introduces a complication when attempting to assess the significance of ionization potential differences. We will not pursue this aspect further here, but in general terms we can at least say that the ionization potential provides a measured indication of the firmness with which an electron is held and accordingly should serve as some guide as to whether an electron can be mobilized for valence purposes or not.

Two ionization potential trends

Two ionization potential trends become apparent when the transition elements are considered according to their location in the Periodic Table. There is a vertical trend (different quantum groups) and a horizontal one (variation within one quantum group) which together may in part account for the variable valence behaviour (number and stability of valence states) of the transition elements.

The vertical trend. It has been pointed out[5] (i) that the ionization potential difference ($\Delta_{2,3}$) between the second 4*s* electron and the first 3*d* electron is much greater than that between the corresponding ionization potentials between 5*s* and 4*d*, and 6*s* and 5*d*; and (ii) that the differences between successive ionization potentials involving 3*d* electrons are greater than those involving successive 4*d* and successive 5*d* electrons. The first observation apparently arises as a result of (ii), because the ionization potentials of *s* electrons in transition elements belonging to the same vertical group are usually not greatly different.[5]

These features correlate quite well with observed valence stability trends in the

Group IV elements, Ti, Zr, Hf, and Th, and in the Group V elements, V, Nb, Ta, and Pa.

The horizontal trend. Two developments may be distinguished when moving along

TABLE 3.—VARIATION OF $\Delta_{2,3}$ FROM Sc TO Zn (for I_2 the average of LANDOLT-BÖRNSTEIN and FINKELNBURG and HUMBACH have been used; for I_3, values have been read off the graph in Fig. 1)

	$\Delta_{2,3}$ (volts)	
Sc	12·0	
Ti	14·3	
V	15·75	
Cr	15·15*	
Mn	18·2	
		half-shell
Fe	14·1	
Co	16·8	
Ni	17·8	
Cu	17·8*	
Zn	22·0	

* I_2 refers to a *d* electron.

the 3*d* quantum group, from Sc to Zn. The first involves the difference between the ionization potentials required to remove the second and third electrons ($\Delta_{2,3}$)—that is, the second 4*s* electron and the first 3*d* electron—and the second involves *d* electrons only.

From Sc to Cu the magnitude of $\Delta_{2,3}$ tends to increase. The trend is, however, not smooth, because (i) of the Mn→Fe half-shell discontinuity, and (ii) because the second ionization potentials of Cr and Cu refer to *d* electrons and not *s* electrons. Variation of $\Delta_{2,3}$ from Sc to Zn is given in Table 3. For detailed comparison of variation of I_2 and I_3 see Fig. 11 of AHRENS[5] and Fig. 1 of this paper, respectively.

The first horizontal trend correlates fairly well with variation of the stability of the divalent state from Sc to Zn.

In the sub-group Sc—Ti—V—Cr—Mn, divalence is absent in Sc, feeble in Ti, V, and Cr, and well developed in Mn. Greater stability of Cr^{II}—say equivalent to Fe^{II}—would be anticipated had the valence-electron structure of Cr been d^4s^2 and not d^5s^1. The low stability of Ti^{II}, V^{II}, and Cr^{II} is due to their tendency to oxidize to higher valencies, and this correlates with their low values of $\Delta_{2,3}$; in Sc, $\Delta_{2,3}$ is still lower and Sc^{II} is nonexistent, as oxidation to Sc^{III} is apparently spontaneous under all conditions.

Fe^{II} is generally less stable than Mn^{II} because of the ease of oxidation of Fe^{II} to Fe^{III}; this may be correlated with the half-shell discontinuity drop of I_3 (Fig. 1). But for this development, Fe^{II} is likely to have been very stable indeed. The stability trend of the divalent state is again apparent in the half-group Fe—Co—Ni—Cu—Zn. Great stability of Zn^{II} is evidently due not only to the general increase of I_3 from Sc to Zn, but also because I_2 drops at Zn (see Fig. 11 of AHRENS[5]), and thus $\Delta_{2,3}$ is sharply elevated to 22 volts (Table 3).

The second ionization potential trend (*d* electrons only) is of particular concern for a study of the higher valencies of the transition elements. As in the first trend, the ionization potential difference between two succeeding *d* electrons increases as we pass from Ti to Zn (Sc has only one *d* electron), as seen in Fig. 2, and this corresponds roughly with increasing difficulty of oxidation to higher valence states.

TABLE 4.—IONIZATION POTENTIALS (VOLTS) OF Mn AND Re

	1	2	3	4	5	6	7	8
	— 4*s* —		—————— 3*d* ——————					
Mn	7·4	15·6	~34	~53	~76	~101	~119	~195
	—— 6*s* ——		—————— 5*d* ——————					
Re	~8	~13	~26	~38	~51	~65	~79	?

The same general trend is noticeable in members of the subsequent 4*d* quantum group, Zr—Nb—Mo—(Tc)—Ru. We recall above that $\Delta_{n,m}$, the ionization potential difference between two succeeding *d* electrons, for 4*d* electrons is less than for 3*d* electrons (given vertical group); and this may be the reason why trivalence in Zr is extremely feeble or absent as compared with Ti. In moving horizontally, however,

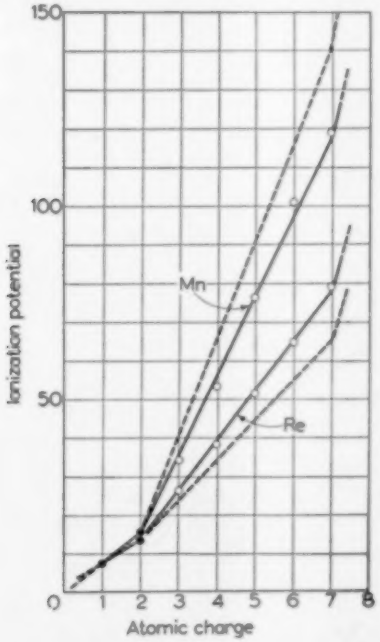

Fig. 4.—Variation of ionization potential with ionic charge in Mn ($3d^5 4s^2$) and Re ($4d^5 5s^2$). The upper and lower dashed lines correspond roughly to slopes obtaining for Zn and Th, respectively. The slope for Fe is slightly greater than that for Mn but considerably less than Zn; that for Ru is between the slopes of Mn and Re.

$\Delta_{n,m}$ increases as in the $3d$ sequence, but by the time Ru is reached, $\Delta_{n,m}$ is not excessively high as in the Fe group; in fact, the magnitudes of $\Delta_{n,m}$ in Ru appear to have reached optimal—neither too low nor too high. Virtually all possible valence states exist and there is no extreme general tendency either to reduce or to oxidize.

Manganese and rhenium

These general correlations may be illustrated further by comparing in greater detail the behaviour of the two group VII elements Mn ($3d^5 4s^2$) and Re ($5d^5 6s^2$). Their estimated ionization potentials[7] are given in Table 4, and though approximate, they nevertheless appear to serve satisfactorily for the general purpose of comparison which we have in mind.

The data of Table 4 are represented graphically in Fig. 4. It is quite clear from Table 4 and from Fig. 4 that the differences in ionization potential when passing from an s to a d electron ($\Delta_{2,3}$) and from d to d (up to $\Delta_{6,7}$) is distinctly greater in Mn even if full allowance is made for uncertainty of some of the data. These differences appear to correlate quite well with the valence properties of these two elements—for example, the high stability of Mn^{II} and doubtful existence of Re^{II}; ease of oxidation of Re to Re^{VII} (extremely stable) compared with greater difficulty of oxidation of Mn to Mn^{VII} (not particularly stable).

Summary of valence trends

The general trends noted above concerning valence states of the transition elements are summarized below. Six groups may be distinguished, and they have been arranged in order of ease of losing d electrons; (Group (i)—electrons most loosely bound, and group (vi)—electrons most firmly bound).

A
- (i) possible lower valence states (i.e. $<$ group valence) absent—Sc, Y, La, Th.
- (ii) possible lower valence states either of very feeble stability or absent—Zr and Hf, (Pa?).

B
- (iii) W, Ta. (Nb, Mo, and Ti).
- (iv) V, Cr. (Nb, Mo, and Ti).
- (v) Mn, Ru, Rh, Re, Os, Ir. (Fe, Pt).

(iii) to (v)—intermediate groups.

Most possible valence states exist; in general, stability at a maximum in (v) where there is no great general tendency either to oxidize or to reduce.

C. (vi) d electrons firmly held, and only lower valence states exist—Co, Ni, Cu, Pd (Fe and Pt). Elements such as Cu, Ag, Au, and also Zn, Cd, and Hg could also be included.

The divisions are not sharp, and overlap is indicated by the elements which have been placed in parenthesis.

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J. Inorg. Nucl. Chem., 1957, Vol. 4, pp. 273 to 278. Pergamon Press Ltd., London

MASS SPECTRAL STUDIES OF TRIMETHYL BORON

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Abstract—The mass spectrum of trimethyl boron is reported and an analysis in terms of contributing ions is given. Methyl migration from one molecule to another is shown not to occur under a wide range of experimental conditions.

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THE preparation of substituted boron hydrides has long been a problem of interest to workers in the field. Alkyl and halogen derivatives of diborane can be readily prepared by exchange with the appropriate borane in many cases, but attempts to carry out similar exchanges with higher boranes have not led to the desired products. It seems probable that the mechanism whereby such exchange reactions take place in the first case is not operative in the case of higher boranes, and a better understanding of the mechanism of exchange with diborane consequently seems desirable.

Although no evidence has yet been acquired to show that alkyl groups can form bridges between two boron atoms, such an intermediate would provide a ready path for exchange by means of equilibria of the type

$$B^{13}C_3H_9 + B^{12}C_3H_9 \rightleftharpoons [B_2{}^{13}C_3{}^{12}C_3H_{18}] \rightleftharpoons B^{13}C_2{}^{12}CH_9 + B^{13}C^{12}C_2H_9 \qquad (1)$$

and the transition complex would be structurally similar to the well-known methyl-bridged $Al_2(CH_3)_6$. This study was undertaken to attempt to provide some evidence for such an intermediate in the case of the simple trialkyl borane.

Vapour density measurements by STOCK and ZEIDLER in 1921 revealed that boron trimethyl was a monomer in the temperature range −25°C to 100°C.[1] Also, LAUBENGAYER in a private communication to PITZER reported that boron trimethyl was a monomer in benzene solution.[2] Studies of the Raman spectrum by GOUBEAU and BECHER in 1952 gave no evidence of a dimer of boron trimethyl at temperatures as low as −100°C.[3] Since these studies were unsuccessful in detecting any evidence of dimerization, a more sensitive method was desirable. If boron trimethyl does dimerize through the formation of methyl bridge bonds, the dimeric structure would provide a path whereby methyl groups could migrate between boron atoms. Analysis of the mass spectra of mixtures of normal trimethyl boron and trimethyl boron containing excess ^{13}C would allow one to determine the extent of methyl migration under various conditions, if it occurred at all. It was necessary first to determine the mass spectrum of boron trimethyl, which apparently had not previously been reported.

EXPERIMENTAL

A vacuum system, similar to that described by R. T. SANDERSON,[4] was used in this investigation for the preparation of the desired compounds. Samples were

[1] A. STOCK and F. ZEIDLER *Ber. Mach. chem. Ges.* **54**, 531 (1921).
[2] K. S. PITZER and H. S. GUTOWSKY *J. Amer. chem. Soc.* **68**, 2204 (1956).
[3] J. GOUBEAU and H. J. BECHER *Z. anorg. Chem.* **268**, 1 (1952).
[4] R. T. SANDERSON *Vacuum Manipulation of Volatile Compounds* John Wiley, New York (1948).

introduced to the system through ground-glass joints and stopcocks lubricated with Dow Corning Silicone or Apiezon "T" greases. Purification procedures were performed using standard fractional condensation techniques. For measuring amounts of gaseous samples, a U-tube equipped with a manometer was calibrated with a weighed amount of carbon dioxide. All analyses were made with a mass spectrometer designed and built by one of us (H. J. S.). The instrument is similar to that described by NIER,[5] having a 60° sector magnet, a radius of 15·0 cm, a conventional ion source such as is used in many gas instruments, and a viscous flow-leak for introducing the sample into the ion source. The ionizing electron current is electronically controlled and regulated. An inverse-feedback electrometer (tube 5800) amplifier employing an input resistor of $8 \times 10^{10}\ \Omega$ is used to detect the ion currents. This amplifier is linear to $\pm$0·25 per cent for ion currents from 10^{-15} to about 10^{19} A. Its noise level was 5×10^{-16} A or less during the measurements. All measurements were made using 70 eV ionizing electrons, 60-μA trap current, and 1800 V ions. Mass scanning was done magnetically. Sample pressure in the reservoir was 2·0 cm.

Two samples of boron trimethyl were prepared by reaction of the methyl Grignard with boron trifluoride etherate. Normal methyl iodide and a sample containing 66 at. per cent ^{13}C, obtained from Eastman Organic Chemical Company, were used in the preparations. Pure boron trimethyl was obtained by fractionation of the crude material through traps maintained at −112°C and −45°C, pure boron trimethyl being retained in the −145°C trap. The calculated vapour pressure of boron trimethyl at −45°C is 248 mm, whereas the observed vapour pressure for the normal boron trimethyl was 247·7 mm, and was 249 mm for the boron trimethyl containing the heavier isotope.

Table 1 presents the complete mass spectrum of normal boron trimethyl, giving the total ion current for each mass number. An analysis of this spectrum in terms of contributing ion species is given in Table 2. Ion currents above mass 56 are comparatively small and can be attributed to the natural isotopic abundance of ^{13}C. A comparison of the 57 and 56 mass currents, assuming ^{13}C to be the sole contributor to the 57 peaks, leads to a value of 0·03 for the atomic fraction of ^{13}C. No further correction has been made in the boron trimethyl mass spectrum for the natural isotopic abundance of ^{13}C. Corrections have been made for carbon dioxide, nitrogen, and water known to be present in the mass spectrometer background. The observed $^{10}B/^{11}B$ ratio was used to calculate the contribution of each lighter ion from that of the heavier, assuming the 56 peak was pure $^{11}B^{12}C_3H_9$. The observed $^{10}B/^{11}B$ ratio leads to an atomic weight of 10·80 for boron, in good agreement with the accepted value of 10·82.

The total of the mass currents appearing at mass numbers 42 and 43 represents approximately 2 per cent of the mass current at mass number 41 and can therefore reasonably be considered as due to naturally occurring ^{13}C. Similarly, the current at mass number 27 is approximately 1 per cent of the peak at 27 is approximately 1 per cent of the peak at 26, and thus can be attributed to ^{13}C.

In the analysis of the mass spectra of samples containing both ^{12}C and ^{13}C in appreciable amounts, the contribution of an ion containing ^{10}B in place of ^{11}B was calculated from the observed $^{10}B/^{11}B$ ratio. The above analysis of the normal boron trimethyl spectrum allowed determination of the relative intensities of ion species

[5] A. O. NIER *Rev. sci. Instrum.* **18**, 398–411 (1947).

TABLE 1.—MASS SPECTRUM OF NORMAL BORON TRIMETHYL

Mass	Mass current*	Mass	Mass current
65	0·001	37	0·710
64	0·001	36	0·252
63	0·000	35	0·031
62	0·000	34	0·003
61	0·000	33	0·000
60	0·001	32	0·001
59	0·002	31	0·001
58	0·002	30	0·001
57	0·007	29	0·018
56	0·193	28	0·287
55	0·050	27	0·004
54	0·003	26	0·352
53	0·063	25	0·103
52	0·019	24	0·017
51	0·077	23	0·002
50	0·147	22	0·002
49	0·137	21	0·000
48	0·055	20	0·000
47	0·009	19	0·000
46	0·002	18	0·065
45	0·005	17	0·018
44	0·127	16	0·198
43	0·013	15	0·260
42	0·179	14	0·038
41	7·500	13	0·138
40	2·013	12	0·047
39	0·889	11	0·174
38	0·337	10	0·042

* An ion current of $1{\cdot}250 \times 10^{-11}$ A is equivalent to 1·000 in this representation.

having lost one or more hydrogen atoms, assuming no effect on carbon-hydrogen bond rupture by the replacement of ^{12}C by ^{13}C. This assumption was found to be valid by STEPHENSON[6] in studies of ^{13}C labelled propane and butane, who reported that the probabilities are essentially equal of the various carbon isotopic molecule ions losing one or more hydrogen atoms to form stripped ions. The remaining ion currents were then calculated by difference.

Table 3 shows the result of application of this method to the ^{13}C enriched sample for the four heaviest masses. Note particularly that for the ions of mass 58 the correction of the $^{10}B^{13}C_3H_9$ ion can be known as accurately as the $^{10}B/^{11}B$ ratio and that the ion $^{11}B^{13}C_3H_8$ contributes only a small amount to the total mass current. Thus, a relatively large error in that ion, even if introduced by an unexpected change in ionization probability, does not appreciably affect the accuracy of measurement of the current due to the remaining ion.

To determine the extent of exchange in a given sample, the effective atomic fraction (EAF) of ^{13}C was determined from the relative abundances of the $^{11}B^{13}C_3H_9$

[6] D. P. STEPHENSON *J. chem. Phys.* **19**, 17 (1951).

TABLE 2.—ANALYSIS OF THE UNIPOSITIVE IONS PRESENT IN THE ISOTOPICALLY NORMAL BORON TRIMETHYL SPECTRUM

Mass	Ion	Ion* current	Mass	Ion	Ion* current
56	$^{11}B^{12}C_3H_9$	0·193	36	$^{10}B^{12}C_3H_2$	0·160
55	$^{10}B^{12}C_3H_9$	0·046		$^{11}B^{12}C_3H$	0·092
	$^{11}B^{12}C_3H_8$	0·004	35	$^{10}B^{12}C_3H$	0·022
54	$^{10}B^{12}C_3H_8$	0·001		$^{11}B^{12}C_3$	0·010
	$^{11}B^{12}C_3H_7$	0·002	34	$^{10}B^{12}C_3$	0·003
53	$^{10}B^{12}C_3H_7$	0·001	33		0·000
	$^{11}B^{12}C_3H_6$	0·063	32		0·001
52	$^{10}B^{12}C_3H_6$	0·015	31		0·001
	$^{11}B^{12}C_3H_5$	0·004	30		0·001
51	$^{10}B^{12}C_3H_5$	0·001	29		0·018
	$^{11}B^{12}C_3H_4$	0·076	28	†	0·287
50	$^{10}B^{12}C_3H_4$	0·018	27	$^{11}B^{13}CH_3$	0·004
	$^{11}B^{12}C_3H_3$	0·129	26	$^{11}B^{12}CH_3$	0·352
49	$^{10}B^{12}C_3H_3$	0·031	25	$^{10}B^{12}CH_3$	0·083
	$^{11}B^{12}C_3H_2$	0·106		$^{11}B^{12}CH_2$	0·020
48	$^{10}B^{12}C_3H_2$	0·025	24	$^{10}B^{12}CH_2$	0·005
	$^{11}B^{12}C_3H$	0·030		$^{11}B^{12}CH$	0·012
47	$^{10}B^{12}C_3H$	0·002	23	$^{10}B^{12}CH$	0·003
	$^{11}B^{12}C_3$	0·007		$^{11}B^{12}C$	0·000
46	$^{10}B^{12}C_3$	0·002	22		0·002
45		0·005	21		0·000
44		0·127	20		0·000
43	$^{11}B^{12}C_2H_6$	0·013	19		0·000
42	$^{10}B^{12}C_2H_6$	0·003	18	H_2O†	0·065
	$^{11}B^{13}C^{12}CH_6$	0·176	17	OH†	0·018
41	$^{11}B^{12}C_2H_5$	7·500	16	CH_4	0·198
40	$^{10}B^{12}C_2H_5$	1·775	15	CH_3	0·260
	$^{11}B^{12}C_2H_4$	0·238	14	CH_2	0·038
39	$^{10}B^{12}C_2H_4$	0·056	13	CH	0·138
	$^{11}B^{12}C_2H_3$	0·832	12	C	0·047
38	$^{10}B^{12}C_2H_3$	0·197	11	B	0·174
	$^{11}B^{12}C_2H_2$	0·140	10	B	0·042
37	$^{10}B^{12}C_2H_2$	0·033			
	$^{11}B^{12}C_2H$	0·676			

* An ion current of $1·250 \times 10^{-11}$ A is equivalent to 1·000 in this representation.
† Represent ion species known to be present in the mass spectrometer background.

and the $^{11}B^{13}C_2{}^{12}CH_9$ ions. In a randomly distributed system where the atomic fraction of ^{13}C is x, the relative abundance of these two ions is

$$B^{13}C_3H_9 = x^3; \qquad B^{13}C_2{}^{12}CH_9 = 3x^2(1 - x).$$

In turn, using measured ion currents for the two ions (corrected as described above), one can obtain the EAF

$$\text{EAF} = x = \frac{3(B^{13}C_3H_9)}{3(B^{13}C_3H_9) + (B^{13}C_2{}^{12}CH_9)}$$

If little or no exchange has taken place, these ions will be in nearly the same relative abundance as in the sample containing 60 per cent ^{13}C, since the standard ^{12}C sample

TABLE 3.—PARTIAL MASS SPECTRUM OF BORON TRIMETHYL CONTAINING 66 PER CENT ^{13}C

Mass	Ion	Mass current	Ion current
59	$^{11}B^{13}C_2H_9$	0·116	0·116
58	$^{10}B^{13}C_2H_9$	0·207	0·026
	$^{11}B^{13}C_2H_8$		0·002
	$^{11}B^{13}C_2{}^{12}CH_9$		0·179
57	$^{10}B^{13}C_2H_8$	0·136	0·001
	$^{11}B^{13}C_2H_7$		0·001
	$^{10}B^{13}C_2{}^{12}CH_9$		0·040
	$^{11}B^{13}C_2{}^{12}CH_8$		0·004
	$^{11}B^{13}C^{12}C_2H_9$		0·091
56	$^{10}B^{13}C_2H_7$	0·075	0·000
	$^{11}B^{13}C_2H_6$		0·037
	$^{10}B^{12}C_2{}^{12}CH_8$		0·001
	$^{11}B^{12}C_2{}^{12}CH_7$		0·002
	$^{10}B^{13}C^{12}C_2H_9$		0·020
	$^{11}B^{13}C^{12}C_2H_8$		0·002
	$^{11}B^{12}C_2H_9$		0·013

contributes no peaks in this region. In a randomly distributed mixture of ions, that is one which has undergone complete exchange, the EAF of ^{13}C would equal the actual atomic fraction (AAF) corresponding to the weighted average isotopic content of the two components of a mixture.

The comparison of the values listed in Table 4 indicates that very little exchange took place in the mixtures, regardless of treatment. The footnotes to Table 4 show the relative pressures in a standard volume of the sample containing 60 per cent ^{13}C and of the sample containing ^{12}C which were mixed to form the sample for studying the exchange reaction, as well as the conditions used for each sample. The EAF values for all samples are close to the AAF value of the 66 per cent ^{13}C sample, indicating that the amounts of the two ions used in calculating the EAF value are essentially those contributed by the pure material. Some EAF values as low as 63 per cent occur, but, since the value does not appear to be time-dependent, they probably provide a crude measure of experimental error.

DISCUSSION

Whereas previous attempts to observe dimeric trimethyl boron were limited to the conclusion that the extent of polymerization was less than perhaps 5 to 10 per cent, the current study shows that essentially no symmetrical dimer is formed even at low temperatures. It is important to observe the limitation that only a symmetrical dimer necessarily leads to methyl exchange.

The recent work of FURUKAWA and PARK[7] on the low-temperature properties of boron trimethyl show that a solid–solid transition takes place at $86{\cdot}5 \pm 0{\cdot}5°K$. The possibility of this transition being caused by a slow dimerization in the solid could not be overlooked, but experiments similar to those reported above were

[7] G. T. FURUKAWA and R. P. PARK *Nat. Bur. Stand. Rep.* 3649 (1954).

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TABLE 4.—CALCULATED AND OBSERVED ATOMIC FRACTIONS OF ^{13}C IN EXCHANGE EXPERIMENTS

Sample	Effective atomic fraction of ^{13}C	Actual atomic fraction of ^{13}C	Mass current 59	Mass current 58
1[a]	0·66	0·41	0·036	0·063
2[b]	0·66	0·41	0·036	0·068
3[c]	0·66	0·41	0·038	0·064
4[d]	0·65	0·31	0·055	0·100
5[e]	0·65	0·35	0·052	0·095
6[f]	0·65	0·35	0·055	0·101
7[g]	0·63	0·30	0·051	0·102
8[h]	0·63	0·27	0·035	0·069
9[i]	0·64	0·30	0·040	0·076
10[j]	0·03	0·01	0·002	0·002
11[k]	0·66	0·66	0·116	0·207

[a] Gas mixture, 56 min; ^{13}C −16·9 mm; ^{12}C −10·5 mm.
[b] Sample 1 cooled 80 min at −135.
[c] Sample 2 cooled ½ hr at −135.
[d] Liquid mixture, 7 hr at −135; ^{13}C −19·9 mm; ^{12}C −21·9 mm.
[e] Gas mixture, 7 hr; ^{13}C −16·7 mm; ^{12}C −15·2 mm.
[f] Sample 5 after standing 1 hr condensed at −135.
[g] Gas mixture, 19 hr; ^{13}C −14·6 mm.
[h] Gas mixture, 81 hr; ^{13}C −13·8 mm; ^{12}C −19·9 mm.
[i] Gas mixture, 82 hr; cooled to −196 for one additional hr; ^{13}C −14·6 mm; ^{12}C −17·7 mm.
[j] Boron trimethyl, normal.
[k] Boron trimethyl containing 66 per cent ^{13}C.

carried out by Mr. JOHN DUPONT and showed that no exchange took place even for samples held in liquid-nitrogen baths for periods as long as 1 week.

The presence of trace amounts of diboranes caused extensive methyl migration in short periods in the trimethyl boron itself, as would be expected from the known interaction of these materials to form the methyl diboranes. No direct evidence has been presented for methyl "bridges" in the methylation of diborane, but this still appears to be the most likely path.

Acknowledgement—Mass spectrometric analyses were obtained through the courtesy and assistance of Mr. J. CAPELLAN and Mr. R. HARRINGTON using the facilities of the Ames Laboratory.

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QUINQUEVALENT COMPOUNDS OF URANIUM—II

URANIUM PENTA-*n*-ALKOXIDES

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Abstract—The quinquevalent uranium compounds $U(OR)_5$, where R = Me, Et, Pr^n, Bu^n, and Am^n, have been prepared and their molecular weights have been determined ebullioscopically in benzene. Boiling points were determined under reduced pressure. These results are discussed from the structural viewpoint, and it is proposed that uranium penta-alkoxides may involve uranium in co-ordination numbers of 6 and 8. The uranium penta-alkoxides are compared with the corresponding derivatives of niobium and tantalum.

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IN A recent communication[1] we described the preparation of the penta-ethoxide and the penta-iso-propoxide of uranium. This paper concerns the preparation of several penta-*n*-alkoxides of uranium, $U(OR)_5$, where R = Me, Et, Pr^n, Bu^n, Am^n, and a study of their structural properties. Our primary objectives in this research were

(a) to produce more new derivatives of quinquevalent uranium, and
(b) to compare their structural properties with those of the corresponding derivatives of niobium and tantalum.

Towards the end of our investigations, GILMAN *et al.*[2] described the preparation of several uranium penta-alkoxides by a variety of methods, and hence the compounds described here can no longer be claimed as new. However, GILMAN *et al.* (*loc. cit.*) did not carry out a systematic study of the structural aspects of these compounds as we have done. In this work, the penta-ethoxide was prepared by the method described previously (*loc. cit.*) which, incidentally, differs from the several methods described by GILMAN *et al.* (*loc. cit.*) The other penta-alkoxides were then obtained by alcohol interchange. The pentamethoxide was a rust-coloured crystalline substance which could be crystallized from methanol and sublimed unchanged at 140–150°/0·01 mm. The other penta-alkoxides were brown mobile liquids which could be distilled under low pressure without either decomposition or disproportionation. The boiling-points of these compounds were determined under the standardized conditions previously described in connection with penta-alkoxides of niobium[3] and of tantalum.[4] Molecular weights were determined ebullioscopically in benzene and the molecular complexities (M_{found}/M_{calc}) and boiling-points are reported in the table together with the data for the corresponding derivatives of niobium and tantalum.

The molecular complexities given in the table reveal interesting structural relationships between niobium, tantalum, and uranium in the quinquevalent state. Except

[1] D. C. BRADLEY, B. N. CHAKRAVARTI, and A. K. CHATTERJEE *J. inorg. nucl. Chem.* **3**, 367 (1957).
[2] R. G. JONES, E. BINDSCHADLER, G. KARMAS, F. A. YOEMAN, and H. GILMAN *J. Amer. chem. Soc.* **78**, 4287 (1956); R. G. JONES, E. BINDSCHADLER, G. KARMAS, G. A. MARTIN JR., J. R. THIRTLE, F. A YOEMAN, and H. GILMAN *Ibid.* 4289.
[3] D. C. BRADLEY, B. N. CHAKRAVARTI, and W. WARDLAW *J. chem. Soc.* 2381 (1956).
[4] D. C. BRADLEY, W. WARDLAW, and A. WHITLEY *Ibid.* 726 (1955).

R in $M(OR)_5$	Boiling-point (°C/mm)			Molecular complexity (degree of polymerization)		
	Nb[3]	Ta[4]	U	Nb[3]	Ta[4]	U
Methyl	153/0·1	130/0·2	140–150/0·01[a]	2·11	1·98	3·01
Ethyl	156/0·05	146/0·15	161/0·05	2·02	1·98	1·90
n-Propyl	166/0·05	184/0·15	181/0·07	2·02	1·95	1·95
n-Butyl	197/0·15	217/0·15	206/0·15	2·01	2·02	1·94
n-Amyl	223/0·15	239/0·2	246/0·05	2·00	2·01	1·94

[a] Sublimes

for uranium pentamethoxide, these penta-alkoxides are all predominantly dimeric. We have previously suggested[4] that the dimeric tantalum penta-alkoxides are examples of 6-co-ordinate tantalum in which the metal atoms are octahedrally surrounded by oxygen atoms and that the dimer molecule consists of two octahedra sharing a common edge. On this basis it appears that quinquevalent uranium in the penta-alkoxides (except the methoxide) is also mainly in the 6-co-ordinated state. The pentamethoxide presents an interesting structural problem because of its considerably higher molecular complexity or degree of polymerization. The 6-co-ordination of uranium could be maintained in a trimeric molecule by adding a third octahedron to the dimer such that the third unit involved the sharing of a common apex. However, this process could be continued indefinitely to produce very high polymers and this would cause a very pronounced variation of molecular weight with concentration. Our ebullioscopic measurements did not reveal any significant variation in molecular weight over the limited range of concentrations studied. It has been suggested* that the pentamethoxide could be a cyclic trimer in which the uranium is still 6-co-ordinate, but in our view the cyclic trimer is sterically more favoured than the dimer and on this basis all of the *n*-alkoxides should be trimeric. We prefer to interpret the results in terms of the suggested principle[5] that the metal in a metal alkoxide tends to assume its maximum covalency with the minimum degree of polymerization of the alkoxide. On this basis, the dimer is the smallest polymer

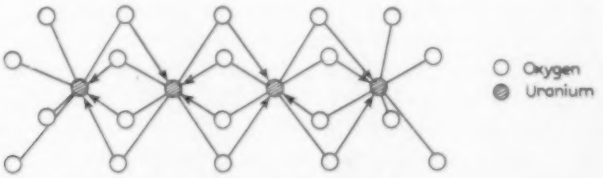

FIG. 1.—$U_4(OR)_{20}$ (R groups omitted).

required for a 6-co-ordinate metal penta-alkoxide. To explain the higher degree of polymerization in the pentamethoxide, we suggest that quinquevalent uranium may attain a maximum covalency of 8. The smallest polymer required to achieve 8-co-ordination (cubic) of uranium in a penta-alkoxide is the tetramer shown in the figure.

* The authors are indebted to one of the referees for making this suggestion.

[5] D. C. BRADLEY *Industr. engng. Chem.* In press.

Accordingly, it is suggested that uranium pentamethoxide contains an appreciable proportion of 8-co-ordinate uranium present in the tetrameric form in equilibrium with dimers containing 6-co-ordinate uranium. It is clear that steric factors will favour the formation of the dimers, and this causes the penta-alkoxides with larger alkyl groups (>methyl) to be predominantly dimeric in boiling benzene solution. It is interesting to note that TAYLOR *et al.*[6] found from cryoscopic measurements in benzene that the degree of polymerization of uranium penta-ethoxide varied from 1·56 (0·0815 molal solution) to 2·38 (1·14 molal solution). Thus it appears that at a lower temperature and much higher concentration than were used in our experiments the penta-ethoxide also contains a significant proportion of 8-co-ordinated uranium.

The data in the table reveal not only the structural similarities between the penta-alkoxides of niobium, tantalum, and uranium, but also similarities in volatilities. This is especially interesting, because the uranium atom is considerably larger than niobium or tantalum atoms and the intermolecular forces in the uranium alkoxides would therefore be expected to be greater than those in the niobium or tantalum alkoxides. In fact, the relative volatilities appear to be: Ethoxides, Ta > Nb > U; *n*-propoxides, Nb>Ta≃U; *n*-butoxides, Nb>U>Ta; *n*-amyloxides, Nb>Ta>U. It would be unwise to attempt to interpret these data in the absence of more detailed vapour pressure studies because of the complicated nature of the vaporization process for these complex molecules. However, it is clear that these data conform to the prediction made elsewhere[7] that similar molecules of this type should be close in volatility, irrespective of the mass of the central metal atom, and that the heavier molecule may sometimes be the more volatile.

We are currently studying the physicochemical properties of uranium penta-alkoxides containing branched alkyl groups, and expect to obtain some monomeric compounds which will be even more suitable for comparison with the corresponding derivatives of niobium and tantalum.

EXPERIMENTAL

The apparatus, technique, and analytical methods were similar to those previously described.[1,3,4]

Uranium penta-ethoxide. This was prepared as before[1] from a reaction involving pyridinium uranium-oxypentachloride (57 g), ethanol (100 g), and ammonia in benzene (320 g) solution. A dark brown mobile distillate (9·4 g) was ultimately obtained. (Found: U 51·4, EtO 48·1%. $U(OEt)_5$ requires: U 51·4, EtO 48·6%.)

Uranium pentamethoxide. The penta-ethoxide (8 g) was refluxed for 3 hours with methanol (70 g) and the cold mother liquor then separated by decantation. The solid uranium compound was recrystallized twice with successive amounts of methanol (300 c.c., 250 c.c.). The prismatic rust-coloured crystals (5 g) were dried for 2 hours at 80°/0·1 mm. (Found: U 60·7, MeO 38·9%. $U(OMe)_5$ requires: U 60·6, MeO 39·4%.)

*Uranium penta-*n*-propoxide.* The penta-ethoxide (13·9 g) was caused to react with *n*-propanol (60 g) in benzene (150 g) solution. The liberated ethanol was removed azeotropically by fractional distillation. After evaporation of the solvent, the uranium *n*-propoxide was distilled *in vacuo* and gave a brown liquid distillate (15·4 g). (Found: U 44·4%. $U(OPr)_5$ requires: U 44·6%.)

[6] T. I. TAYLOR, E. R. SMITH, J. L. TORGESEN, H. MATHESEN, and J. K. TAYLOR *A.E.C.D.*-3144.
[7] D. C. BRADLEY *Nature, Lond.* **174,** 323 (1954).

*Uranium penta-*n*-butoxide.* The pentamethoxide (3·3 g) was caused to react with *n*-butanol (50 g) in benzene (150 c.c.) solution and the liberated methanol was separated by azeotropic distillation. After evaporation of the benzene, the uranium penta-*n*-butoxide was obtained as a mobile brown liquid distillate (4·4 g). (Found: U 39·5%. $U(OBu)_5$ requires: U 39·4%.)

*Uranium penta-*n*-amyloxide.* The penta-*n*-propoxide (12·3 g) was caused to react with *n*-amyl alcohol (50 c.c.) in benzene (150 c.c.) in the usual manner and the penta-*n*-amyloxide was isolated as a viscous brown distillate (13·7 g). (Found: U 35·5%. $U(OAm)_5$ requires: U 35·3%.)

Molecular weights. These were determined in a specially modified Menzies-Wright ebulliometer, using previously described methods.[1,3,4] Agreement was obtained between results obtained by the external calibration method using azobenzene and by the internal calibration method using fluorene. None of these uranium compounds showed any significant variation of the apparent molecular weight with concentration. Some typical results are given in the following table.

R in $U(OR)_5$	Range of weights of solute (g)	Weight of benzene (g)	Slope $\Delta T°$/g solute	M.W.	
				Found	Calc.
Methyl	0·0238–0·1370	14·70	0·1650	1218	393·2
Ethyl	0·2848–0·6172	15·64	0·2125	882	463·4
n-Propyl	0·0338–0·3708	17·28	0·1665	1018	533·5
n-Butyl	0·0336–0·2748	14·47	0·1740	1164	603·6
n-Amyl	0·0253–0·1832	13·83	0·1625	1314	673·8

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SOME COMPLEX CHLORIDES OF URANIUM TETRACHLORIDE AND THORIUM TETRACHLORIDE*

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(*Received* 26 *November* 1956)

Abstract—The preparation of the five anhydrous complex chlorides $[(CH_3)_4N]_2UCl_6$, $[(C_2H_5)_4N]_2UCl_6$, Cs_2UCl_6, $[(CH_3)_4N]_2ThCl_6$, and Cs_2ThCl_6 is described. The results of powder X-ray diffraction studies of these compounds are given, and the possibility of hydrates existing for the thorium complexes is discussed.

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THE complex chlorides of uranium tetrachloride of the type M_2UCl_6 where M is an alkali metal, tetramethylammonium or tetraethylammonium have been reported.[1–6] Confirmatory studies are lacking, and there exists some question as to the purity of these compounds, inasmuch as analytical data for the most part are not included in these reports. The literature on the complex chlorides of thorium tetrachloride of the type M_2ThCl_6, where M is an alkali metal, appears confused.[7–14] There is considerable disagreement as to whether the anhydrous chloride or oxychloride is formed. Analytical data are also lacking in much of this work. The complex chlorides of thorium tetrachloride with tetramethylammonium chloride or with tetraethylammonium chloride have not been reported. In addition, X-ray work on these compounds has been neglected, except for recent studies with the di-(tetramethylammonium) and di-(tetraethylammonium) uranium hexachlorides.[5] It was thus believed of interest to devote further study to some of these compounds. This paper confirms the preparation of the anhydrous salts $[(CH_3)_4N]_2UCl_6$, $[(C_2H_5)_4N]_2UCl_6$, Cs_2UCl_6, Cs_2ThCl_6, and describes for the first time the preparation of $[(CH_3)_4N]_2ThCl_6$.

EXPERIMENTAL

Materials

(a) Uranium tetrachloride was made from pure $UO_2(NO_3)_2 \cdot 6H_2O$ (Mallinckrodt Co.) by chlorination with hexachloropropene[15] and was subsequently twice resublimed in a vacuum; (b) thorium tetrachloride (99%), whose commercial source was not known, was obtained from the

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

(1) H. MOISSAN *Compt. rend.* **122**, 1088 (1896).
(2) J. ALOY *Bull. Soc. chim.* **21**, 264 (1899).
(3) J. ALOY *Ann. Chim. Phys.* (7) **24**, 412 (1901).
(4) G. H. DIEKE and A. B. F. DUNCAN *Spectroscopic Properties of Uranium Compounds* McGraw-Hill Book Co. Inc., New York, N.Y.
(5) E. STARITZKY and J. SINGER, Atomic Energy Commission Document 3071 (Feb. 26, 1951).
(6) E. STARITZKY and A. L. TRUITT, Atomic Energy Commission Document 3017 (March 16, 1950).
(7) J. J. BERZELIUS *Svenska Akad. Handl.* **1**, (1829). *Pogg. Ann.* **16**, 385 (1829).
(8) J. J. CHYDENIUS *Pogg. Ann.* **119**, 43 (1863).
(9) P. T. CLEVE *Bull. Soc. chim.* (2) **21**, 115 (1874).
(10) L. F. NILSON *Ber.* **15**, 2537 (1882).
(11) G. KRÜSS and W. PALMAER *Z. anorg. Chem.* **14**, 361 (1897).
(12) H. MOISSON and O. HÖNIGSCHMIDT *Ann. Chim. Phys.* (8) **8**, 182 (1906).
(13) H. L. WELLS and J. H. WILLIS *Amer. J. Sci.* (4) **12**, 191 (1901).
(14) E. CHAUVENET *Ann. Chim. Phys.* (8) **23**, 425 (1911).
(15) J. J. KATZ and E. RABINOWITCH *The Chemistry of Uranium*, National Nuclear Energy Series, Div. VIII, Vol. 5. Part 1, p. 468. McGraw-Hill Book Co., Inc. (1951).

Special Materials Division of Argonne National Laboratory; (c) caesium chloride was C.P. grade from Sargent and Co.; (d) tetramethylammonium chloride (98–99%) was obtained from Matheson Co.; (e) tetraethylammonium chloride (94%) was from RSA Corp., Ardsley, New York.

Analyses

Water analyses were determined by standard Karl Fischer titration.[16] Chloride analyses were made by standard gravimetric procedures and by the Volhard volumetric method.[17] Uranium was determined by precipitation with ammonium hydroxide and subsequent ignition of the ammonium uranate to U_3O_8.[18] Thorium was determined by precipitation as the hydroxide and ignition to thoria (ThO_2).[19] Caesium was determined by precipitation as the perchlorate.

Procedure

A mixture of 25 g of uranium tetrachloride and 18·7 g of tetramethylammonium chloride (30% excess over stoichiometric amount) was dissolved in 200 ml 4 M hydrochloric acid (freshly distilled and diluted with boiled distilled water) in a 1 litre, three-neck flask. The flask was fitted with a separatory funnel, a fritted-glass filter stick, and an outlet to a mechanical vacuum pump. The filter stick was lowered and the solution was drawn through it into a second 1 litre three-neck flask also containing the above-mentioned attachments. The solution was then vacuum-distilled to a 20 ml volume. The supernatant liquid was drawn off through the filter stick. Additional acid was added to dissolve the solid and the crystallization procedure repeated. The apparatus used permitted filtering and transferring without exposure to air. The wet solid was dried by evacuation at 105°C for 32 hours. The final pumping was done on a vacuum line at 105°C and 10^{-3} mm pressure for 8 hours. The solid obtained was stored in a sealed, evacuated bulb. Alternatively, the wet solid could be dried at room temperature in a vacuum desiccator over concentrated sulphuric acid at 0·2 cm pressure for 1–2 weeks. Quantitative yields of the anhydrous chloride were obtained.

The method described above for the preparation of di-(tetramethylammonium) uranium hexachloride is the general method used in preparing all the anhydrous compounds described in this paper with the following exceptions:

(1) Stoichiometric amounts of caesium chloride were used in the preparations of dicaesium uranium hexachloride and dicaesium thorium hexachloride.

(2) The drying of the thorium complex chlorides was done in a vacuum desiccator over concentrated sulphuric acid at 0·2 cm pressure for 1 month.

Precautions must be taken in the preparation of the uranium complex chlorides to prevent oxidation, and for this reason the preparation is done entirely in a vacuum. In addition, the uranium tetrachloride used in the preparation must be free of uranyl chloride, for the uranyl complex chloride formed from it is a contaminant difficult to remove.

DISCUSSION AND RESULTS

(a) *Anhydrous complex chlorides of* UCl_4 *and* $ThCl_4$

The anhydrous complex uranium salts are a light green colour. Water is taken up by these salts only slowly, and hydrates are not formed according to powder X-ray results.

The anhydrous complex thorium salts are milky white, and they pick up water more rapidly than the uranium salts. In contrast to the uranium salts, hydrates are formed.

The analytical data for these salts are presented in Table 1.

The complex chlorides of uranium tetrachloride and thorium tetrachloride containing the tetramethylammonium group appear to be stable to 150°. Beyond this temperature they begin to decompose, giving off an amine odour. Between 360° and

[16] J. MITCHELL JR. and C. M. SMITH *Aquametry* Interscience Publishers, Inc., New York (1948).
[17] C. J. RODDEN *Analytical Chemistry of the Manhattan Project* National Nuclear Energy Series, Div. VIII Vol. 1. p. 292. McGraw-Hill Book Co., Inc. (1950).
[18] *Ibid.* p. 47.
[19] *Ibid.* p. 183.

TABLE 1.—ANALYTICAL DATA FOR SOME COMPLEX CHLORIDES OF UCl_4 AND $ThCl_4$

	% Cl		% U		% Th		% Cs		% H_2O	Mole ratio
Compound	Theor.	Found	Theor.	Found	Theor.	Found	Theor.	Found	Found	Cl/A[a]
$[(CH_3)_4N]_2UCl_6$	35·51	35·48	39·74	39·72	—	—	—	—	nil[b]	6·00
$[(C_2H_5)_4N]_2UCl_6$	29·91	29·78	33·47	33·41	—	—	—	—	nil	5·99
Cs_2UCl_6	29·69	29·46	33·22	33·18	—	—	37·09	36·86	nil	5·96
$[(CH_3)_4N]_2ThCl_6$	35·87	35·85	—	—	39·13	39·30	—	—	nil	5·97
Cs_2ThCl_6	29·94	29·72	—	—	32·65	32·40	37·41	—	0·26	6·00

[a] *A* is uranium or thorium atom.
[b] Nil is considered 0·1% or less.

400° these complexes char. If heated rapidly, they will take fire. Dicaesium uranium hexachloride melts at 425° ± 10°. Anhydrous dicaesium thorium hexachloride appears to show some decomposition at 580°–600° with no melting.

(b) *Powder X-ray diffraction studies*

Some results of powder X-ray diffraction studies on these preparations are summarized in Table 2. A more detailed paper on the X-ray diffraction studies of these complexes containing caesium has been published.[20] The report[5] that di-(tetramethylammonium) uranium hexachloride crystallizes in a face-centred cubic structure like di-(tetramethylammonium) plutonium hexachloride,[21] was confirmed. That the substitution of ethyl for methyl changes the symmetry to an orthorhombic form[5] was verified. The crystal structure of dicaesium uranium hexachloride was determined and found to be trigonal and isostructural with dicaesium plutonium hexachloride.[22]

TABLE 2.—POWDER X-RAY CRYSTALLOGRAPHIC RESULTS

Compound	Symmetry	Number of molecules per unit cell	Density (X-ray) g/cm³
$[(CH_3)_4N]_2UCl_6$	Face-centred cubic	4	1·788
$[(C_2H_5)_4N]_2UCl_6$	Orthorhombic	4	1·69
Cs_2UCl_6	Trigonal	1	4·030
$[(CH_3)_4N]_2ThCl_6$	Face-centred cubic	4	1·83[a]
Cs_2ThCl_6	Trigonal[b]	1	3·87

[a] Method of displacement of helium gas.
[b] Converts to this structure upon standing.

The uranium atom is bonded to six chlorines at a distance of 2·75 Å. Each caesium has twelve chlorine neighbours with the Cs-Cl distance, being on an average 3·70 Å. The wet intermediate solids isolated for each of the above uranium salts were found to have the

[20] S. SIEGEL *Acta cryst. Camb.* **9**, 827 (1956).
[21] H. H. ANDERSON *Dicesium Plutonium (IV) Hexachloride and Related Compounds* Paper 6.13 in SEABORG, KATZ, and MANNING *Transuranium Elements* National Nuclear Energy Series, Div. IV, Vol. 14B. Part I pp. 793–795 McGraw-Hill Book Co., Inc. (1949).
[22] W. H. ZACHARIASEN *Acta cryst. Camb.* **1**, 268 (1948).

same X-ray powder diffraction pattern as the anhydrous compounds. Therefore it is very unlikely that a hydrate system exists for the uranium compounds.

Anhydrous di-(tetramethylammonium) thorium hexachloride was found to be isostructural with di-(tetramethylammonium) uranium hexachloride. Anhydrous dicaesium thorium hexachloride when freshly prepared was found to have a structure which is not like that of dicaesium uranium hexachloride. However, upon standing, the structure converts to the trigonal form of Cs_2UCl_6, in which the thorium atoms are bonded to six chlorines at a distance of 2·81 Å and the average Cs-Cl distance is 3·7 Å. The trigonal structure is also obtained for the solid produced by the fusion of 1 mole of $ThCl_4$ and 2 moles of CsCl.

(c) *Possible hydrates of the complex chlorides of* $ThCl_4$

Powder X-ray diffraction patterns have indicated the possibility that hydrates exist for di-(tetramethylammonium) thorium hexachloride and dicaesium thorium hexachloride, since the intermediate solids isolated for these thorium salts were found to have powder X-ray diffraction patterns different from those of the anhydrous solids. With di-(tetraethylammonium) thorium hexachloride, very wet solids were obtained (one with 27% water), and these could only be dried to a water content of 6%. Long periods of desiccation failed to dry them further. A sample of di-(tetramethylammonium) thorium hexachloride crystallized with close to 3 moles of water per thorium. Analyses—Found: Th 35·46%, Cl 32·78%, H_2O 9·09%, Cl/Th = 6·05. A sample of dicaesium thorium hexachloride crystallized with close to 9 moles of water per thorium. Analyses—Found: Th 26·64%, Cl 26·18%, H_2O 19·65%, Cl/Th = 6·43.

Acknowledgments—The author wishes to thank Dr. STANLEY SIEGEL for the X-ray diffraction data; KENNETH J. JENSEN and IRENE M. FOX for some of the analytical data; and Dr. DARRELL W. OSBORNE for many valuable suggestions.

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SALTS OF HYDRAZINETETRASULPHONIC ACID

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(*Received* 18 *March* 1957)

Abstract—Tetrapotassium hydrazinetetrasulphonate has been prepared by the electrolytic oxidation of tripotassium aminedisulphonate (imidodisulphate) in aqueous solution. Platinum, graphite, and lead oxide anodes are effective. In the case of platinum, increased conversions are obtained in the presence of fluoride ion up to the solubility limit. Both N_2 gas and NO_2^- ion are formed as higher oxidation products of nitrogen.

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HYDRAZINEMONOSULPHONATES and symmetrical hydrazinedisulphonates have been known for some time[1,2] and have usually been prepared from hydrazine and a sulphonating agent, such as SO_3-pyridine. Recently the preparation of salts of unsymmetrical hydrazinedisulphonic acid from hydroxylamine-O-sulphonic acid and dipotassium aminedisulphonate (imidodisulphate) was reported.[3] It was mentioned that this compound could be further sulphonated to produce the tri- and tetrasulphonates, but no details were given.*

It is the purpose of this communication to describe the preparation of salts of hydrazinetetrasulphonic acid by electrolytic oxidation of aminedisulphonate salts in aqueous solution. The postulated anode reaction is:

$$2[N(SO_3)_2]^{3-} \rightarrow 2e^- + [(SO_3)_2N - N(SO_2)_3]^{4-}$$

Platinum, lead oxide, and graphite were all effective as anode materials. The presence of fluoride ion was found to be beneficial when a platinum anode was used, and this system was studied in more detail. Besides the hydrazinetetrasulphonate, both N_2 gas and NO_2^- ion were detected as higher oxidation products of nitrogen.

EXPERIMENTAL

Electrolyses were carried out in open vessels using a platinum-wire cathode contained in a porous diaphragm of glass, alundum, or paper. Sheets or rods of various materials were used as anodes. Trisodium and tripotassium aminedisulphonates were prepared by displacing ammonia from the triammonium salt[4] with aqueous sodium or potassium hydroxide, followed by crystallization of the salt from solution. The trisodium salt used in most of the work was obtained directly in this

* Note added in proof:
A referee has called attention to a subsequent publication by MEUWSEN and TISCHER [*Angew. Chem.* **68**, 385 (1956)] in which further details were given. In their procedure the unsymmetrical hydrazinedisulphonate is converted to the trisulphonate with pyridine-SO_3. In alkaline solution the trisulphonate undergoes a kind of disproportionation, forming azodisulphonate, $[SO_3N{=}N{-}SO_3]^{=}$, and hydrazinetetrasulphonate $[(SO_3)_2N{-}N(SO_3)_2]^{=}$.

(1) L. F. AUDRIETH and B. A. OGG *The Chemistry of Hydrazine* pp. 220–2 John Wiley, New York (1951).
(2) L. F. AUDRIETH and S. F. WEST *J. Amer. chem. Soc.* 77, 5000 (1955).
(3) A. MEUWSEN and H. TISCHER *Angew. Chem.* **67**, 617 (1955)

manner. It was more convenient to crystallize the dipotassium aminedisulphonate, which is only sparingly soluble, and to dissolve it in a stoichiometric quantity of potassium hydroxide, than to prepare the solid tripotassium salt. Both the sodium and potassium compounds were free of sulphates and ammonium compounds.

Solutions 0·2 to 0·5 M in aminedisulphonate, containing varying amounts of the corresponding fluoride, were electrolysed under various conditions of temperature, current density, and pH. Hydrazine was originally identified as a product by acidifying and boiling the solutions to hydrolyse the sulphonates, followed by precipitation as salicylaldazine and determination of its melting-point. The above preparation and a sample of salicylaldazine prepared from hydrazine hydrochloride, as well as a mixture of the two, all melted sharply at 218°C (uncorr.). Hydrazine was determined quantitatively after hydrolysis by iodimetric titration at pH 7.[5]

Tetrasodium hydrazinetetrasulphonate was moderately soluble in these systems, but at the higher conversions it crystallized out of the cell solution and could be isolated. The tetrapotassium salt was only slightly soluble, and was easily isolated as a white crystalline solid by filtration. A complete analysis of one such product, after drying in a desiccator, gave:

	Weight %		Mole ratio
	Calculated	Determined	
K	30·94	30·1	4·11
SO_3	63·51	63·2	4·22
N–N (hydrazine)	5·55	5·24	1·00
N (ammonia)	—	0·04	
		98·6	

Potassium was determined by flame photometry, and SO_3 was determined as sulphate after hydrolysis. Ammonia nitrogen was determined by the Kjeldahl method.

The solubility of the tetrapotassium salt in water at 27° ± 1°C was determined to be 0·0054 M (2·7g/1.). The solution is neutral and gives no precipitate with $BaCl_2$. Such solutions decolourize alkaline permanganate and reduce ammoniacal silver solution readily, but decolourize iodine only slowly. The tetrasulphonate is hydrolysed to hydrazine within 15 min in boiling 1N acid.

No hydrazinetetrasulphonate was found when a copper anode was used. With anodes of platinum, graphite, and lead oxide at a current density of approximately 15 mA/cm², conversions of 4, 15, and 30 per cent, respectively, of the aminedisulphonate to hydrazine tetrasulphonate were observed. It was soon found that the presence of fluoride ion increased markedly the conversions at a platinum anode, and for simplicity most experiments were done with this system. Fluoride had been reported to raise the oxygen overvoltage on platinum,[6] and was expected to suppress the formation of oxygen as a side reaction. No conversion was obtained at either lead or platinum anodes when the ammonium salt was used in place of the sodium or potassium salts.

[4] *Inorganic Syntheses* Vol. 2, p. 180. McGraw Hill, New York.
[5] Reference (1), p. 160.
[6] S. GLASSTONE and A. HICKLING *Electrolytic Oxidation and Reduction* p. 64. Van Nostrand, New York (1936).

A few preliminary runs indicated that to obtain good conversions, the temperature should be kept below 30–40°C. The pH of the initial aminedisulphonate solution, which is about 10 for a 0·2 M solution, appeared to be optimum. Experiments in 0·1 M OH^- and at pH 7 gave poor conversion to hydrazine.

DISCUSSION

In Table 1 are presented some of the data on the effect of current density, time, and fluoride concentration on the current efficiencies and conversions. The current efficiency

TABLE 1.—EFFECT OF FLUORIDE CONCENTRATION, CURRENT DENSITY, AND TIME ON CURRENT EFFICIENCY AND CONVERSION. INITIAL AMINEDISULPHONATE CONCENTRATION 0·2 M, EXCEPT EXPERIMENT 37, IN WHICH IT WAS 0·5 M. PLATINUM ANODE, AMBIENT TEMPERATURE, pH DURING RUNS *c.* 8–10

Experiment no.	Fluoride conc. (g F^-/l.)	Current density (mA/cm^2)	Duration (min)	Current efficiency* (%)	Conversion to N_2H_4† (%)
		Sodium system			
10	0·25	15	60	14·5	14·5
1	1·0	15	60	28	28
9	5·0	15	60	37	37
12	5·0	30	30	26	26
11	5·0	60	15	21	21
13	5·0	15	30	34	17
14	5·0	15	120	16	32
15	5·0	15	240	10	39
		Potassium system			
16	5·0	15	60	9	9
17	25	15	60	19	19
20	50	15	60	15	15
19	80	15	60	38	38
34	50	15	60	37	15

* Current efficiency $= \frac{\text{current used to produce } N_2H_4}{\text{total current passed}}$

† Conversion $= \frac{\text{nitrogen converted to } N_2H_4}{\text{total nitrogen in original material}}$

decreases with increasing current density. This is to be expected for dilute solutions of reactant, because the desired electrode process tends to become diffusion-limited as the current density increases, with the result that the current increase goes largely into oxygen liberation from the water. Conversion to hydrazine tetrasulphonate increases with time, although the overall current efficiency decreases. This effect is attributed to a decrease in the aminedisulphonate concentration as the electrolysis progresses, with the result that oxidation of water or of the hydrazinetetrasulphonate tends to become predominant.

The effect of fluoride is shown more clearly in Fig. 1 for both the sodium and potassium systems. In each case, the curves were extended to the solubility limits of the system. Curiously, the same maximum conversions were achieved in each case, although the ratio of fluoride concentrations was 16 : 1.

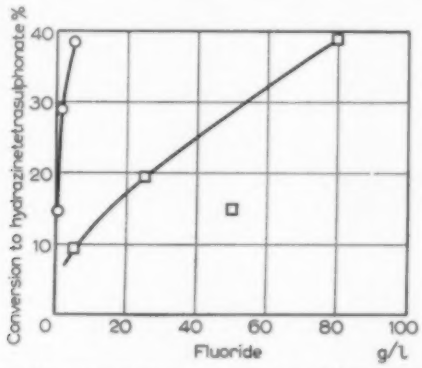

FIG. 1.—Effect of fluoride concentration on conversion. 0·2 M aminedisulphonate, platinum electrodes, current density 15 mA/cm², duration 60 min.
○ Sodium salt □ Potassium salt

Aside from the liberation of oxygen, further oxidation of nitrogen also occurs. Nitrogen gas was identified as a product by carrying out an electrolysis in a closed system in a slow stream of argon gas, in which the nitrogen was determined mass-spectrometrically. Near the beginning of the run the N_2 : H_2 ratio was 1 : 16, while near the end it was 1 : 1·4. Because of the high current density, the cathode product is principally hydrogen at all times. The increase in N_2 formation during the run suggests, therefore, that N_2 is produced by oxidation of the product, hydrazinetetrasulphonate, rather than directly from the reactant, aminedisulphonate. Nitrite was detected qualitatively here, and in other experiments by the rapid oxidation of iodide at pH 1–2, and was determined also by reduction to NH_3, followed by distillation and titration.

Although not fully explained, one other aspect of the electrolysis deserves mention. Because the tribasic aminedisulphonate ion is derived from a weak acid,[7] it may be titrated with acid to an end-point at a pH of about 7. Titrations before and after electrolysis usually showed that titratable base had disappeared during the experiment. The overall reaction for the formation of hydrazinetetrasulphonate is:

$$2[N(SO_3)_2]^{3-} + 2\,H_2O \rightarrow [(SO_3)_2N{-}N(SO_3)_2]^{4-} + 2\,OH^- + H_2$$

Since two equivalents of titratable base are used up and two more are formed, along with a neutral salt, no net change in titre should occur as a result of the above reaction. In most experiments, it was found that one mole of base disappeared for each mole of nitrogen not accounted for as NH_3 of N_2H_4 derivatives. The formation of N_2 or NO_2^- would require the loss of 2 or 3 moles of base, respectively, per mole of nitrogen unaccounted for. It appears likely that there is some other product formed which has not been detected, but which is involved in the change in base titre.

The author gratefully acknowledges the assistance of Mr. H. O. KERLINGER, who carried out many of the chemical analyses.

[7] G. S. DOYLE and N. DAVIDSON *J. Amer. chem. Soc.* **71**, 3491 (1949).

J. Inorg. Nucl. Chem., 1957, Vol. 4, pp. 291 to 295. Pergamon Press Ltd., London

THE HEAT OF FORMATION OF GALLIUM TRICHLORIDE-PHOSPHORUS OXYCHLORIDE

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Abstract—The design of an all-glass precision calorimeter for measurement of the heats of reaction of hygroscopic or reactive substances in an inert atmosphere is described. The estimated total error to be expected in a determination is ±0·5–1%; the observed reproductibility in the present experiments is ±0·1%.

The heat of hydrolysis of phosphorus oxychloride was found to be 79·60 ± 0·05 kcal mole^{-1}, in good agreement with other recent determinations of this quantity. The heat of formation of crystalline gallium trichloride-phosphorus oxychloride from crystalline gallium trichloride and liquid phosphorus oxychloride at 25·0° was found to be 10·1$_7$ ± 0·01 kcal mole^{-1}; this corresponds to a standard heat of formation from the elements of $-\Delta H_f^\circ = 280{\cdot}0$ kcal mole^{-1}. The heat of formation in the gas phase from monomeric gallium trichloride and phosphorus oxychloride is 22·6 kcal mole^{-1}.

THE energies involved in electron donor-acceptor reactions and the heat of formation of crystalline molecular addition compounds and other complex co-ordination compounds can be measured directly in those cases where one of the components is a liquid, the other being either solid, liquid, or gas. For example, when the ligand (L) is a liquid and the acceptor (A) a solid, the heat of formation may be found by subtracting from the heat of reaction of the acceptor in excess of the ligand, an amount equal to the heat of solution of the complex itself (AL_n) in the ligand to give the same total concentration:

$$A\,(c) + (x + n)L(l) = AL_n \text{ (dissolved in } x \text{ moles of } L);\ -\Delta H_1$$

$$AL_n(c) + xL(l) = AL_n \text{ (dissolved in } x \text{ moles of } L);\ -\Delta H_2$$

$$\therefore\ A\,(c) + nL(l) = AL_n(c);\ -\Delta H_3 = -\Delta H_1 + \Delta H_2.$$

It is clearly immaterial whether the solution of the complex is ionized, dissociated, or solvated, provided only that in both reactions the same final state is achieved.

Many inorganic compounds which take part in such reactions are volatile, hygroscopic, or readily oxidized, and the systems have consequently been little studied. A calorimeter was therefore designed which would be capable of working in an inert atmosphere over a range of temperatures. The instrument has so far been used successfully both for reactions involving complexes of the gallium trihalides and for the measurement of heats of aquation and ammination of transition-metal ions, but it may also be readily applied to a variety of other chemical reactions.

EXPERIMENTAL

Calorimeter

The mixing vessel, shown approximately to scale in Fig. 1, was made from a B55 cone and measured 4·5 × 17 cm internally. It had an outer vacuum jacket sealed on about 2 cm below the ground joint to decrease heat-losses. The calorimeter head was a B55 socket rounded off about 2 cm from the

grinding; it carried six attachments *A–F*. *A* and *B* were mercury-sealed inlets, one of which carried the stirrer and the other a glass breaker rod. Both seals incorporated guide tubes, the one for the breaker rod continuing right down into the calorimeter, where it also served to position the glass ampoule *G*. The seal allowed for a vertical movement of about 3 cm for the breaker rod without the baffle rising out of the mercury. *C* and *D* were B10 cones, one of which (*D*) carried a drip-feed and was used to add the donor liquid; the other inlet was for dry nitrogen. No tap-grease was used, the

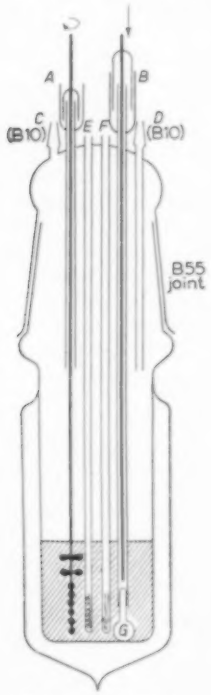

FIG. 1.—Calorimeter

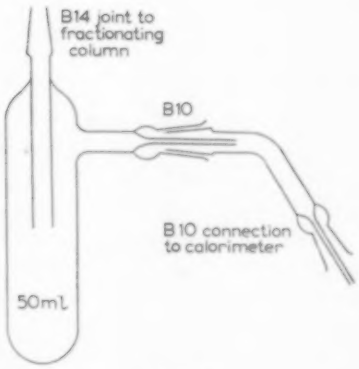

FIG. 2

cones being covered with "Teflon" B10 sleeves. *E* and *F* were wells of specially thinned glass for the calibration heater and thermocouple respectively.

The calorimeter was charged in the following way. The head was inverted, a bulb (*G*) containing a known amount of substance was fitted into the breaker guide tube, and the mixing vessel lowered into position. The apparatus was then reinverted into its normal position, the mercury seals filled, and the breaker rod inserted. The ligand was added by distilling the previously purified liquid into the vessel shown in Fig. 2, which was then fitted onto the feed tube (*D*) and inverted. The whole assemblage was placed in a large Dewar vessel, which was itself contained in a well-stirred thermostat controlled at 25·0° ± 0·1° by a contact thermometer and cold-cathode valve relay. Finally, the calorimeter was swept out with scrupulously dried nitrogen for about 20 min after which time B10 caps were placed on the cones.

The ligand, which was also the calorimetric liquid, was stirred by a glass rod carrying two 1·5 cm paddles and a terminal screw. The stirrer was driven at 160 r.p.m. by gearing down one of the thermostat-bath stirrers. Preliminary experiments had shown that this stirring rate gave efficient mixing with negligible heat of stirring.

Electrical circuits

Temperature was measured by means of a 15-junction copper-constantan thermocouple connected to a Pye Vernier precision potentiometer reading to 1 μV; by interpolation, the galvanometer deflection gave the thermo-emf to $<0{\cdot}5$ μV (0·0008°).

The heating circuit was of standard design. The heater coil, made from 36-gauge "Eureka" wire and having a total resistance of about 5 ohm, was accurately standardized by comparison with a 10-ohm substandard guaranteed to 0·05%. Current was taken from three large-capacity 2 V batteries in series and was passed through a dummy heater of similar resistance to that of the calibration heater for at least 3 hours before a run to steady it. During calibration heating, the voltage varied by less than 1 in 20,000. The current drawn was usually about 0·6 A, but this could be varied so as to get a similar temperature-rise in different liquids. The duration of electrical heating (2 min) was timed by means of a stop-watch reading to 0·1 sec, synchronization being facilitated by having an electrical switch of the "press-on" type with a similar movement to that of the stop-watch. All other switches were of the mercury-contact type in order to eliminate contact potentials and resistances. Connections were soldered wherever possible.

Procedure of run and assessment of errors

After the calorimeter had been filled, lagged, and connected to the potentiometer, the system was left for at least 4 hours to attain thermal equilibrium. The run was commenced by taking readings in a fore-period of 10–15 min, during which time the temperature seldom drifted by more than 0·001° per minute. The bulb was broken by a sharp jab from the plunger, and temperature readings were taken every 30 sec for 10 min and then every minute for a further 15–20 min. The temperature-rise was usually complete after 2 min. The liquid was then heated electrically for 2 min for calibration and the temperature followed in a similar way.

The results were plotted graphically and extrapolated to the midpoint between the mixing time and the time to reach the highest point of the temperature rise. The fore-period was normally linear and therefore easy to extrapolate; the upper curve usually had a preliminary hump due to stirring lags and was extrapolated from its linear portion further down. The extrapolation method for the calibration heating run was similar. Rises of 200–300 μV were aimed at for heating, as this minimized extrapolation errors and also gave a linear fall of temperature after the heating had been discontinued.

The following table sets out the principal sources of error together with an estimate of their maximum and their probable magnitude:

	max. error	probable error
Timing (2 × 0·1 sec) in 120 sec	0·2%	0·1%
Standards and potentiometer	< 0·05%	< 0·05%
Weighing (2 × 0·2 mg) in 0·2 g	0·2%	0·1%
Thermometry (2 × 1 μV) in 200 μV	1·0%	0·5%
Total error (r.m.s.)	1·04%	0·52%

The observed precision in the heat of formation of gallium trichloride-phosphorus oxychloride was 0·1%, but from the magnitude of some of the quantities measured it would seem that this reproducibility was partly fortuitous.

Materials

Phosphorus oxychloride, gallium trichloride, and gallium trichloride-phosphorus oxychloride were prepared and/or purified as previously described.[1] Known weights of phosphorus oxychloride were distilled and poured into the calorimeter by the technique outlined above. Gallium trichloride and the complex were loaded into thin-walled bulbs of about 2-cm diameter in a dry box under an atmosphere of dry nitrogen. They were weighed at this time also. In some earlier experiments the bulbs were loaded by vacuum techniques, the weight of the contents being determined by weighing the bulb full before an experiment and then weighing the pieces collected in a sintered-glass crucible after the experiment. Both techniques gave the same results, but the earlier method was more cumbersome and suffered from the further disadvantage that the weight of the reacting material and hence its concentration could not be determined until the end of the experiment. The method was also more susceptible to error if all the glass fragments were not recovered. However, the vacuum-loading technique must be used in those cases where the compound is so reactive or volatile that dry-box techniques are inadequate.

[1] N. N. Greenwood and K. Wade *J. chem. Soc.* (1957).

RESULTS AND DISCUSSION

In order to test the design of the calorimeter, the heat of hydrolysis of phosphorus oxychloride was determined at 25·0° by breaking ampoules of phosphorus oxychloride under distilled water and measuring the temperature rise. The results are summarized in Table 1; the value obtained for the heat of hydrolysis, $79{\cdot}6_0$ kcal mole^{-1}, is in good agreement with the value of $79{\cdot}9 \pm 0{\cdot}3$ kcal mole^{-1} recently obtained by NEALE and WILLIAMS.[2]

TABLE 1.—$POCl_3(l)$ + excess $H_2O(l) = H_3PO_4(aq) + 3HCl(aq)$

Wt. of H_2O	Wt. of $POCl_3$	Mole ratio	ΔT (μV)	Calibration (cal per μV)	$-\Delta H$(kcal mole^{-1})
87 g	0·4780 g	1550 : 1	544	0·4564	$79{\cdot}5_6$
86 g	0·0580 g	12650 : 1	66·5	0·4498	$79{\cdot}6_4$

Data for the heat of reaction of gallium trichloride in excess phosphorus oxychloride at 25·0° are given in Table 2, and similar data for the heat of solution of the complex are presented in Table 3.

TABLE 2.—$GaCl_3(c)$ + excess $POCl_3(l) = GaCl_3{\cdot}POCl_3$ (in excess $POCl_3$)

Wt. of $POCl_3$	Wt. of $GaCl_3$	Mole ratio	ΔT (μV)	Calibration (cal per μV)	$-\Delta H$(kcal mole^{-1})
200 g	0·2445 g	940 : 1	97·0	0·1577	$11{\cdot}0_1$
150 g	0·0964 g	1610 : 1	56·5	0·1066	$11{\cdot}0_9$

By difference, the heat of formation of the complex is:

$$GaCl_3(c) + POCl_3(l) = GaCl_3{\cdot}POCl_3(c);\ -\Delta H = 10{\cdot}1_7 \pm 0{\cdot}01 \text{ kcal mole.}^{-1}$$

The standard heat of formation of crystalline $GaCl_3{\cdot}POCl_3$ from its elements in their standard states may be obtained by combining the experimental heat of formation with the heats of formation of the reacting components:[3,2]

$$Ga(c) + 3/2Cl_2(g) = GaCl_3(c); \qquad -\Delta H_f^\circ = 125{\cdot}4 \text{ kcal mole}^{-1}$$

$$\tfrac{1}{4}P_4(c) + \tfrac{1}{2}O_2(g) + 3/2Cl_2(g) = POCl_3(l); \qquad -\Delta H_f^\circ = 144{\cdot}4 \text{ kcal mole}^{-1}$$

$$GaCl_3(c) + POCl_3(l) = GaCl_3{\cdot}POCl_3(c); \qquad -\Delta H = 10{\cdot}2 \text{ kcal mole}^{-1}$$

$$\therefore\ \tfrac{1}{4}P_4(c) + Ga(c) + \tfrac{1}{2}O_2(g) + 3Cl_2(g) = GaCl_3{\cdot}POCl_3(c); \qquad -\Delta H_f^\circ = 280{\cdot}0 \text{ kcal mole}^{-1}.$$

The heat of formation of the complex in the gas phase can be obtained if the relevant heats of vaporization and sublimation can be measured. The heat of sublimation of gallium trichloride[4] and the heat of vaporization of phosphorus

[2] E. NEALE and L. T. D. WILLIAMS *J. chem. Soc.* 4535. (1952).
[3] W. KLEMM and H. JACOBI *Z. anorg. Chem.* **207**, 177 (1932).
[4] A. W. LAUBENGAYER and F. B. SCHIRMER *J. Amer. chem. Soc.* **62**, 1578 (1940).

TABLE 3.—$GaCl_3 \cdot POCl_3$ (*c*) + excess $POCl_3$(*l*) = $GaCl_3 \cdot POCl_3$ (in excess $POCl_3$)

Wt. of $POCl_3$	Wt. of $GaCl_3 \cdot POCl_3$	Mole ratio	ΔT(μV)	Calibration (cal per μV)	$-\Delta H$(kcal mole^{-1})
100 g	0·3646	590 : 1	10·5	0·0877	$0·8_3$
100 g	0·3100	690 : 1	9·0	0·0881	$0·8_4$

oxychloride[5] are known, but the heat of sublimation of the complex is difficult to measure because of its very low vapour pressure. Unpublished observations[6] indicate an approximate value of 15 ± 3 kcal mole^{-1} for the heat of sublimation of the complex, and this is consistent with a value deduced by EYRING's method from the activation energy of viscous flow of the molten complex.[1] (Activation energy of viscous flow, 3·4 kcal mole^{-1}, should be about one-third to one-quarter of the heat of vaporization of the liquid, which is therefore estimated to be about 10–14 kcal mole^{-1}; to this value a few kcals should be added for the heat of fusion, giving a value close to the approximate experimental figure of 15 kcal mole^{-1}.) Hence:

$$GaCl_3(c) + POCl_3(l) = GaCl_3 \cdot POCl_3(c); \qquad -\Delta H = \quad 10·2 \text{ kcal mole}^{-1}$$

$$GaCl_3(c) = \tfrac{1}{2}Ga_2Cl_6(g); \qquad -\Delta H = -8·5 \text{ kcal mole}^{-1}$$

$$POCl_3(l) = POCl_3(g); \qquad -\Delta H = -8·4 \text{ kcal mole}^{-1}$$

$$GaCl_3 \cdot POCl_3(c) = GaCl_3 \cdot POCl_3(g); \qquad -\Delta H \simeq -15 \text{ kcal mole}^{-1}$$

$$\therefore \quad \tfrac{1}{2}Ga_2Cl_6(g) + POCl_3(g) = GaCl_3 \cdot POCl_3(g); \qquad -\Delta H \simeq 12·1 \text{ kcal mole}^{-1}$$

This implies that the Cl→Ga bond in the complex is 12 kcal stronger than the sum of the two bridging Cl→Ga bonds in the Ga_2Cl_6 dimer. A truer indication of the strength of the donor-acceptor bond may be obtained by calculating the heat of the reaction between $POCl_3$ and the $GaCl_3$ monomer:

$$\tfrac{1}{2}Ga_2Cl_6(g) = GaCl_3(g); \qquad -\Delta H = -10·5 \text{ kcal}^{[7]}$$

Hence $$GaCl_3(g) + POCl_3(g) = GaCl_3 \cdot POCl_3(g); \qquad -\Delta H = 22·6 \text{ kcal mole}^{-1}.$$

It should be remembered, however, that this energy does not reside solely in the Cl→Ga bond, since all the other bonds in the donor and acceptor moieties become modified during complex formation. These results will be compared with those obtained on other systems involving Group III trihalides in subsequent papers.

Acknowledgements—The authors thank the Royal Society for a grant to defray the expenses of the electrical equipment, the Chemical Society for a grant to purchase gallium, and the D.S.I.R. for a maintenance grant to P. G. P.

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THE SELF-REDUCTION OF AMERICIUM(V) AND (VI) AND THE DISPROPORTIONATION OF AMERICIUM(V) IN AQUEOUS SOLUTION

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Abstract—The kinetics of the self-reduction of Am(V) and Am(VI) have been studied in perchloric acid. A mechanism is postulated which accounts for the nonappearance of Am(III) during the simultaneous self-reduction of Am(V) and Am(VI) in dilute acid solutions. Am(IV), produced by the disproportionation of Am(V) in moderately concentrated perchloric acid solutions, is reduced to Am(III) and does not react with Am(V). The decrease in the value of the rate constant for the self-reduction of Am(VI) with increasing sulphuric acid concentration, is shown to be due to the increase in the rate of disproportionation of Am(V).

STUDIES on the self-reduction of Am(VI) and Am(V) have indicated that the reaction is due to the reducing species present in solution from the alpha-particle bombardment of water.[1,2,3] It is expected that Am(VI) and Am(V) in the same solution would undergo simultaneously self-reduction with a consequent increase in concentration of Am(III). Results have shown that the increase in concentration of Am(III) is negligible while Am(VI) remains in solution,[2,3] suggesting that competing reactions are occurring.

Am(V) is believed to disproportionate in moderately concentrated acid according to reaction (1).[3,4]

$$2\text{Am(V)} \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} \text{Am(VI)} + \text{Am(IV)} \qquad (1)$$

This reaction is followed by reactions (2) and (3).

$$\text{Am(IV)} + \text{Am(V)} \underset{k_2'}{\overset{k_2}{\rightleftharpoons}} \text{Am(VI)} + \text{Am(III)} \qquad (2)$$

$$\text{Am(IV)} \xrightarrow{k_3} \text{Am(III)} \qquad (3)$$

The Am(III)/Am(IV) potential has been estimated to be $-2{\cdot}4$ volts. Am(IV) presumably reacts rapidly with water to yield Am(III). Accompanying the disproportionation reaction of Am(V) are the self-reduction reactions of Am(VI) and Am(V).

$$\text{Am(VI)} \xrightarrow{k_4} \text{Am(V)} \qquad (4)$$

$$\text{Am(V)} \xrightarrow{k_5} \text{Am(IV)} \qquad (5)$$

Reactions (2) and (3) are competing, and a determination of the ratio, n, of Am(V)

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[1] L. B. ASPREY, S. E. STEPHANOU, and R. A. PENNEMAN *J. Amer. chem. Soc.* **73**, 5715 (1951).
[2] L. B. ASPREY and S. E. STEPHANOU AECU—924 (1950).
[3] G. N. YAKOVLEV and V. N. KOSYAKOV *Int. Conf. on Peaceful Uses of Atomic Energy, Geneva* Vol. 7. p. 363 (1955).
[4] S. E. STEPHANOU, L. B. ASPREY, and R. A. PENNEMAN AECU—925 (1950).

consumed to Am(III) produced, will determine which reaction predominates. Reactions (1) and (2) will give a value of $n = 3$ and reactions (1) and (3) a value of $n = 2$. YAKOVLEV *et al.*[3] calculated $n = 3$ for the disproportionation of Am(V) in 2 and 4 M sulphuric acid solution, but the equation derived for the calculation of n ignored the self-reduction of Am(V) which must accompany the disproportionation reaction. It is doubtful whether the conclusions of these authors are valid. Values of n have been redetermined in perchloric acid.

The change in the colour of a solution of Am(VI) from straw-yellow in nitric acid to red-brown in sulphuric acid solution,[1] the increase in potential of the Am(V)–Am(VI) couple in going from nitric to sulphuric acid solution[5] and electromigration experiments,[3] indicate that Am(VI) forms complexes in sulphuric acid. This explanation has been given by YAKOVLEV *et al.*[3] for their observation that the rate of self-reduction of Am(VI) decreases with increasing sulphuric acid concentration, but it will be shown that this is essentially incorrect.

EXPERIMENTAL

The 811 mμ ($\varepsilon = 63$), 715 mμ ($\varepsilon = 55$), and 992 mμ ($\varepsilon = 75$) absorption peaks were used to study the concentration of Am(III), Am(V), and Am(VI) respectively in perchloric acid. Spectrophotometric measurements were made at room temperature (18°–25°C), using a Unicam spectrophotometer (Model S.P. 500). Americium of purity greater than 99·5% was used. The only impurities detected were 0·1% magnesium and 0·1% silicon.

Am(V) was prepared by the method of WERNER and PERLMAN,[6] using ozone as the oxidizing agent. $KAmO_2CO_3$[7] thus prepared was dissolved in 0·2 M perchloric acid. To study the disproportionation of Am(V) in 4·5 and 5·5 M perchloric acid, the $KAmO_2CO_3$ complex was dissolved in 0·2 M perchloric acid and 72% perchloric acid was added until the solution was of the required molarity. Am(VI) was prepared by the ozone oxidation of Am(V) in 0·2 M perchloric acid at 95°C.[8] In order to examine the changes in the rate of self-reduction of Am(VI) with increasing concentrations of sulphuric acid, an accurate knowledge of the extinction coefficient for the 992 mμ peak at each acid concentration was required. The spectrum of Am(VI) was therefore studied from 450 to 1000 mμ at acid concentrations varying from 0·1 to 6·0 M in sulphuric acid. The self-reduction reactions of Am(V) and Am(VI) were followed spectrophotometrically. A small concentration of Am(III) and Am(V) was present at the beginning of the study of the self-reduction of Am(VI).

RESULTS AND DISCUSSION

The self-reduction of Am(V) *and* Am(VI) *in* 0·2 M *perchloric acid solution*

In the study of the self-reduction of Am(V), no products other than Am(III) were observed. A plot of the concentrations of Am(V) and Am(III) versus time was linear (Fig. 1), indicating a zero-order reaction with respect to Am(V) and Am(III). Rates measured at various americium concentrations showed a first-order dependence on the total americium concentration, as expected if the self-reduction is due to the reducing species present from the alpha-particle bombardment of water. Values for the rate-constant (k_5) were calculated from the rate law $-d[\mathrm{Am(V)}]/dt = k_5[\mathrm{Am}_T]$, where $[\mathrm{Am}_T]$ is the total americium concentration. The results are shown in Table 1.

A study of the self-reduction of Am(VI) (Fig. 2) showed that the decrease in Am(VI) concentration was linear with time, indicating a zero-order reduction with

[5] R. A. PENNEMAN and L. B. ASPREY AECU—936, (1950).
[6] L. B. WERNER and I. PERLMAN *J. Amer. chem. Soc.* 73, 495 (1951).
[7] J. P. NIGON, R. A. PENNEMAN, E. STARITZKY, T. K. KEENAN, and L. B. ASPREY, *J. chem. Phys.* **58**, 403 (1954).
[8] T. K. KEENAN and S. E. STEPHANOU LADC—1144 (1952).

TABLE 1

Total americium concentration (mM/litre)	$-d$[Am(V)]/dt (mM/litre hour)	$+d$[Am(III)]/dt (mM/litre hour)	k_5 (hr^{-1})
2·6	0·030	0·031	0·0116
5·6	0·068	0·070	0·0121
8·0	0·100	0·090	0·0125

Mean value 0·012 ± 0·005 hr^{-1}

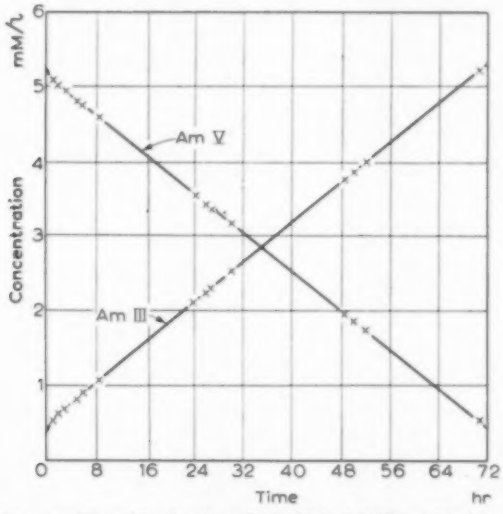

FIG. 1.—The self-reduction of Am(V) in 0·2 M perchloric acid.

respect to Am(VI). Variation of the rate of self-reduction of Am(VI) with total americium concentration showed it to be proportional to the latter. Values for the rate-constant ($k_{4_{obs}}$) for the self-reduction of Am(VI) were calculated from the equation $-d[\text{Am(VI)}]/dt = k_{4_{obs}}[\text{Am}_T]$. The results are shown in Table 2.

When the concentration of Am(VI) had decreased to 1 mM, a small increase in the concentration of Am(III) was observed, accompanied by a decrease in the rate of

TABLE 2

Total americium concentration (mM/litre)	$-d$[Am(VI)]/dt (mM/litre hour)	$k_{4_{obs}}$ (hr^{-1})
3·71	0·11	0·030
4·80	0·14	0·030
8·00	0·25	0·032

Mean value 0·031 ± 0·001 hr^{-1}

growth of Am(V). After the self-reduction of Am(VI) was complete, Am(V) reduced linearly with time to Am(III). The rate-constant for this reduction was calculated to be 0·013 hr^{-1}, which is in good agreement with the value of 0·012 hr^{-1} shown in Table 1.

To account for the observation that the concentration of Am(III) does not increase while Am(VI) remains in solution, it is suggested that Am(VI) reacts with

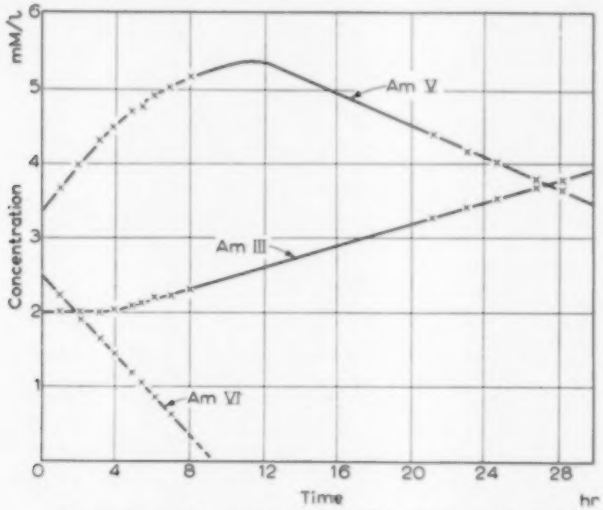

FIG. 2.—The self-reduction of Am(VI) in 0·2 M perchloric acid.

Am(IV) to give Am(V). It has been shown[3,4] that Am(V) undergoes a reversible disproportionation reaction to give Am(VI) and Am(IV) in moderately concentrated acid. The disproportionation of Am(V) is proportional to the fourth power of the hydrogen-ion concentration[4]

$$2AmO_2^+ + 4H^+ \longleftrightarrow AmO_2^{++} + Am^{4+} + 2H_2O.$$

It is probable that in dilute acids, the direction will be mainly that of the reverse reaction. Am(IV) has not been detected in solution and, presumably, reactions (2) and (3) are fast. The observed rate of reduction of Am(VI) is due to a combination of reactions (1–5). From the rate equations for Am(VI) and Am(IV), it will be shown that the observed rate-constant for the reduction of Am(VI) is a combination of the rate-constants for reactions (4) and (5).

As Am(IV) has not been detected in solution, the rate of its formation and removal are equal. The rate laws for Am(IV) and Am(VI) can be written thus:

$$+d[\text{Am(IV)}]/dt = k_1[\text{Am(V)}]^2 + k_5[\text{Am}_T] + k_2'[\text{Am(VI)}][\text{Am(III)}] - [\text{Am(IV)}]\{k_1'[\text{Am(VI)}] + k_2[\text{Am(V)}] + k_3\} = 0$$

$$\therefore \quad [\text{Am(IV)}] = \{k_1[\text{Am(V)}]^2 + k_5[\text{Am}_T] + k_2'[\text{Am(VI)}][\text{Am(III)}]\}/\{k_1'[\text{Am(VI)}] + k_2[\text{Am(V)}] + k_3\} \qquad (6)$$

$$-d[\text{Am(VI)}]/dt = k_2'[\text{Am(VI)}][\text{Am(III)}] + k_4[\text{Am}_T] - k_1[\text{Am(V)}]^2 + [\text{Am(IV)}]\{k_1'[\text{Am(VI)}] - k_2[\text{Am(V)}]\} \qquad (7)$$

When the concentration of Am(VI) is high, no change in the concentration of Am(III) is observed, indicating that reactions (2) and (3) do not occur. Hence

$$k_1'[\text{Am(VI)}][\text{Am(IV)}] \gg k_3[\text{Am(IV)}],\ k_2'[\text{Am(VI)}][\text{Am(III)}], \text{ and } k_2[\text{Am(V)}][\text{Am(IV)}]$$

$$\therefore \qquad [\text{Am(IV)}] = \{k_1[\text{Am(V)}]^2 + k_5[\text{Am}_T]\}/k_1'[\text{Am(VI)}]$$

and

$$-d[\text{Am(VI)}]/dt = k_4[\text{Am}_T] - k_1[\text{Am(V)}]^2 + [\text{Am(IV)}] \cdot k_1'[\text{Am(VI)}]$$
$$= (k_4 + k_5)[\text{Am}_T] = k_{4_{obs}}[\text{Am}_T]$$

Hence, the rate-constant (k_4) for the self-reduction of Am(VI) is $0{\cdot}019 \pm 0{\cdot}002$ hr^{-1}, using the values for $k_{4_{obs}}$ and k_5 given above.

At concentrations of Am(VI) below 0·7 mM, ASPREY[2] observed that the plot of the concentration of Am(VI) versus time departed from linearity. The spectrophotometer used in the present work was too insensitive to measure extremely low

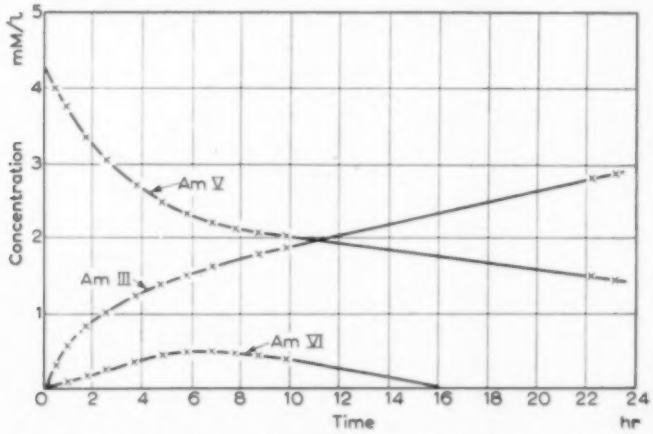

FIG. 3.—The disproportionation reaction of Am(V) in 5·5 M perchloric acid.

concentrations of Am(VI), and this deviation from linearity was not observed. The departure from linearity at low concentrations of Am(VI) is predicted by equations (6) and (7). When the concentrations of Am(VI) is low, the concentration of Am(III) increases, indicating that reactions (2) and (3) are occurring. $k_1'[\text{Am(VI)}][\text{Am(IV)}]$ becomes comparable with $k_3[\text{Am(IV)}]$ and $k_2[\text{Am(V)}][\text{Am(IV)}]$, and $-d[\text{Am(VI)}]/dt$ becomes dependent on the concentration of Am(III) and Am(V).

The disproportionation reaction of Am(V) in 4·5 and 5·5 M perchloric acid

Am(V) disproportionates in moderately concentrated acids to Am(VI) and Am(III) (Fig. 3). A plot of the reciprocal of the concentration of Am(V) versus time gives a straight line for the first 2 hours of the disproportionation indicating a second-order reaction. The plot then deviates from linearity and becomes concave to the time-axis (Fig. 4). The rate equation for the disappearance of Am(V) is $-d[\text{Am(V)}]/dt = k_1[\text{Am(V)}]^2 + (k_5 - k_4)[\text{Am}_T] - k_1'[\text{Am(IV)}][\text{Am(VI)}]$. As the concentration of Am(V) decreases, $(k_5 - k_4)[\text{Am}_T] - k_1'[\text{Am(IV)}][\text{Am(VI)}]$ becomes comparable with $k_1[\text{Am(V)}]^2$ and the plot of $1/[\text{Am(V)}]$ versus time departs from linearity.

The value of n was calculated assuming the following reactions

$$n\ \text{Am(V)} \underset{R_2}{\overset{R_1}{\rightleftharpoons}} (n-1)\ \text{Am(VI)} + \text{Am(III)}$$

$$\text{Am(VI)} \xrightarrow{R_3} \text{Am(V)}$$

$$\text{Am(V)} \xrightarrow{R_4} \text{Am(III)}$$

where $R_1 - R_4$ are the rates of reaction in moles per hour. The rates of formation of Am(III) and Am(VI) will be

$$+d[\text{Am(III)}]/dt = R_1 - R_2 + R_4$$

$$+d[\text{Am(VI)}]/dt = (n-1)(R_1 - R_2) - R_3$$

from which, as R_3 and R_4 equal $k_4[\text{Am}_T]$ and $k_5(\text{Am}_T]$ respectively,

$$n = \{[\text{Am(VI)}] + \text{Am(III)}] + [\text{Am}_T]t(k_4 - k_5)\}/\{[\text{Am(III)}] - [\text{Am}_T]t\,.\,k_5\}$$

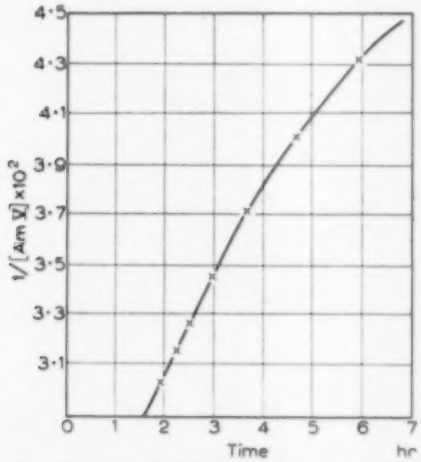

FIG. 4.—1/Am(V) versus time plot for the disproportionation reaction of Am(V) in 5·5 M perchloric acid.

A value of $n = 1{\cdot}3$ to $1{\cdot}7$ was calculated soon after the commencement of the experiments, increasing to a constant value of $n = 1{\cdot}9 \pm 0{\cdot}2$ after several hours. The value of $1{\cdot}9 \pm 0{\cdot}2$ was obtained more quickly for the disproportionation of Am(V) in 4·5 M than in 5·5 M perchloric acid. A determination of n using the results of STEPHANOU *et al.*[4] for the disproportionation of Am(V) in 6 M perchloric acid gave a value of 2·4 at the beginning of the experiment, decreasing to 2·0 after several hours. The values calculated for n indicate either that steady-state conditions are not attained for several hours after the commencement of the experiment, and that at the steady-state reaction (3) occurs in preference to reaction (2), or that a reaction is occurring which has not been considered in the derivation of n.

The self-reduction of Am(VI) in perchloric and sulphuric acids

Measurements of the absorption spectrum of Am(VI) in sulphuric acid (Fig. 5) showed that the major absorption band at 992 mμ and the minor absorption band at 666 mμ, observed in perchloric acid, had shifted to 997·5 mμ and 669 mμ respectively

in 0·1 M sulphuric acid. A second minor peak, not previously observed, appeared at 763·5 mμ. In 6 M sulphuric acid, the 997·5 mμ and 669 mμ peaks underwent a further shift to 998 mμ and 671 mμ. No significant difference in the value of the extinction coefficient (ε) for the 669-mμ peak occurred but ε for the 997·5 mμ and 763·5 mμ peaks altered appreciably as the acid concentration increased. The general ultra-violet absorption below 550 mμ decreased markedly as the acid concentration increased.

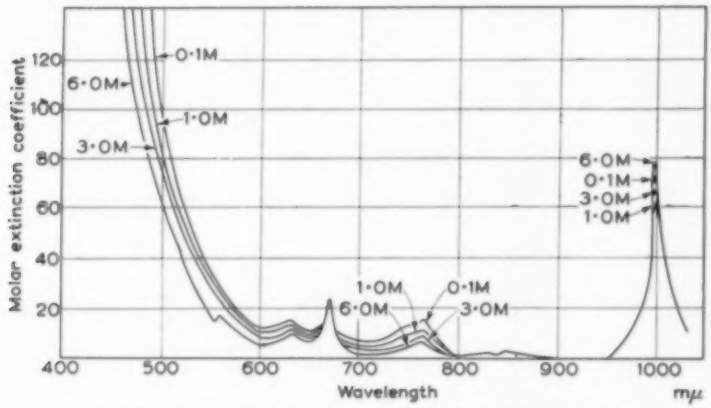

FIG. 5.—The absorption spectrum of Am(VI) in sulphuric acid.

The values of the rate-constant for the self-reduction of Am(VI) with increasing acid concentration are shown in Table 3. In one experiment in 9 M perchloric acid, an abnormally high value (0·016 hr^{-1}) was obtained for the rate-constant.

TABLE 3

Acid	$k_{s_{obs}}$ (hr^{-1})
0·1 M H_2SO_4	0·029
0·5 M H_2SO_4	0·025
3·0 M H_2SO_4	0·017
4·5 M H_2SO_4	0·013
6·5 M H_2SO_4	0·012
9·0 M H_2SO_4	0·012
0·2 M $HClO_4$	0·030
9·0 M $HClO_4$	0·016
9·0 M $HClO_4$	0·013
9·0 M $HClO_4$	0·013

In 0·1 M sulphuric acid, the self-reduction of Am(VI) was accompanied by an increase in concentration of Am(V), but no significant increase in concentration of Am(III) was observed until the Am(VI) had undergone complete self-reduction. The self-reduction of Am(VI) in 3 M sulphuric acid was accompanied by an increase in concentration of both Am(V) and Am(III). In 4·5 M sulphuric acid and 9 M

perchloric acid, the decrease in concentration of Am(VI) was accompanied by an increase in concentration of Am(III). No trace of Am(V) was found in solution.

The rate-constant for the self-reduction of Am(VI) in sulphuric acid decreases with increasing acid concentration in agreement with the observations of YAKOVLEV *et al.*,[3] but a similar trend was observed in perchloric acid. The latter acid is a poor complexing agent and little complex formation between Am(VI) and perchlorate ions would be expected. This indicates that the decrease in the rate of reduction of Am(VI) in sulphuric acid is not due to complex ion formation. The decrease in the rate-constant can be explained by a consideration of the disproportionation reaction of Am(V). The rate-constant for the reduction of Am(VI) can be calculated, assuming that the rate of formation and removal of Am(V) are equal in concentrated acid. Am(V) was not observed in concentrated acid solutions.

$$+d[\mathrm{Am(V)}]/dt = k_2'[\mathrm{Am(VI)}][\mathrm{Am(III)}] + \{k_1'[\mathrm{Am(VI)}] - k_2[\mathrm{Am(V)}]\}[\mathrm{Am(IV)}] - k_1[\mathrm{Am(V)}]^2 - (k_5 - k_4)[\mathrm{Am}_T] = 0$$

$$\therefore \quad \{k_1'[\mathrm{Am(VI)}] - k_2[\mathrm{Am(V)}]\}[\mathrm{Am(IV)}] = k_1[\mathrm{Am(V)}]^2 + (k_5 - k_4)[\mathrm{Am}_T] - k_2'[\mathrm{Am(VI)}][\mathrm{Am(III)}] \qquad (8)$$

By combining equations (7) and (8),

$$-d[\mathrm{Am(VI)}]/dt = k_5[\mathrm{Am}_T]$$

This shows that in concentrated acid, in which Am(V) spontaneously disproportionates the rate-constant for the disappearance of Am(VI) equals the rate-constant for the self-reduction of Am(V). The experimental results are in agreement with this prediction.

Acknowledgements—The authors wish to thank Mr. F. T. BIRKS for many spectrographic analyses and Dr. A. G. WHITE for help with the kinetic equations.

J. Inorg. Nucl. Chem., 1957, Vol. 4, pp. 304 to 314. Pergamon Press Ltd., London

TRI-*n*-BUTYL PHOSPHATE AS AN EXTRACTING SOLVENT FOR INORGANIC NITRATES—II

YTTRIUM AND THE LOWER LANTHANIDE NITRATES

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Abstract—Tri-*n*-butyl phosphate (TBP) can be used to extract and separate yttrium and the lower lanthanides (lanthanum-gadolinium). Extraction from nitric acid solutions generally increases with acidity, sometimes very steeply, though there is often a region of falling partition coefficients between say 4 and 7 M HNO_3. Extraction at low acidity but high nitrate ion concentration (added, for example, as sodium nitrate) is usually high.

Extractability increases with atomic number in the lanthanide series, with yttrium more extractable than any lanthanide at acidities $>c.$ 5 M HNO_3, though less extractable at low acidities. The separation factors for successive lanthanides increase with acidity and reach values as high as 2. They are also high in systems of low acidity but high nitrate concentration, and in presence of TTA (thenoyltrifluoracetone) in the organic phase.

Experiments at varying TBP concentrations indicate the formation of $Y(NO_3)_3 \cdot 3TBP$ and $Ce(NO_3)_3 \cdot 3TBP$. (See also note added in proof.)

THE trivalent rare-earth nitrates are moderately well extracted by TBP, and very high partition coefficients indeed can be obtained under suitable conditions. Moreover, there is sufficient gradation in extractability along the lanthanide series to obtain good separations of the different elements. Solvent extraction using TBP must be considered a serious rival of ion exchange for this purpose.[1] On the other hand, with sufficiently dilute TBP, conditions are readily found such that the rare earths remain behind when uranium or plutonium is extracted. Yttrium, cerium, and other rare-earth fission products may thus be removed from fissile materials.

The present paper is concerned with yttrium and with the trivalent lanthanides from lanthanum to gadolinium, i.e. up to the point where the 4*f* shell is half-filled. The literature[2–12] already contains results for all these elements, though often of rather limited scope because the main aim has been a practical separation process. Our work extends the information available, covering all the elements in question except samarium and gadolinium. We have used effectively trace concentrations (<0·01 M) of the rare earths throughout.

[1] J. M. FLETCHER Paper No. 2, *Extraction and Refining of the Rarer Metals* Institute of Mining and Metallurgy, London (1957).
[2] D. F. PEPPARD, J. P. FARIS, P. R. GRAY, and G. W. MASON *J. Phys. Chem.* **57**, 294 (1953).
[3] D. F. PEPPARD, P. R. GRAY, and M. M. MARKUS *ANL-WMM*-989 (1953?).
[4] A. C. TOPP *ORNL*-1409 (1952).
[5] B. WEAVER, F. A. KAPPELMANN, and A. C. TOPP *J. Amer. chem. Soc.* **75**, 3943 (1953).
[6] A. C. TOPP and B. WEAVER *ORNL*-1811 (1954).
[7] B. WEAVER *Electromagnetically Enriched Isotopes and Mass Spectrometry* p. 86. (Ed. M. L. SMITH) Butterworths, London (1956).
[8] J. F. SUTTLE and J. F. STAMPFER *Prog. Rep. No.* 12, *Contract SC*-5 Univ. of New Mexico (1954).
[9] J. F. SUTTLE and A. POSKANZER *Prog. Rep. No.* 13, *Contract SC*-5, Univ. of New Mexico (1955).
[10] J. G. CUNINGHAME, P. SCARGILL, and H. H. WILLIS *A.E.R.E. C/M* 215 (1954).
[11] R. H. BLACKMORE, A. E. BEARSE, and G. D. CALKINS *BMI*-261 (1952).
[12] J. BOCHINSKI, M. SMUTZ, and F. H. SPEDDING *ISC*-348 (1953); see also R. A. FOOS and H. A. WILHELM *ISC*-695 (1954).

The combined data show that under given conditions (acidity, TBP concentration, etc.) the partition or distribution coefficients

$$D_{La},\ D_{Ce},\ D_{Pr} \ldots D_{Gd}$$

form an approximately geometrical series. That is to say,

$$D_{Ce} = SD_{La}$$
$$D_{Pr} = S^2 D_{La}$$
$$\cdots\cdots\cdots\cdots$$
$$D_{Gd} = S^7 D_{La}$$

where S is the separation factor (ratio of distribution coefficients) for an adjacent pair of elements. In general, $D = S^{Z-57} D_{La}$, where Z is the atomic number, or

$$\log D = Z \log S + \text{constant} \qquad (1)$$

A relation of this form was first proposed by PEPPARD, FARIS, GRAY, and MASON.[2]

It is found in practice that good separation factors can be obtained both at high acidities, when S may be as high as 2, and at a low acidity with a high nitrate-ion concentration. Systems of both types have therefore been studied.

EXPERIMENTAL

The techniques employed were similar to those described in Part 1 of this series.[13]

To facilitate analysis, radioactive isotopes of the rare earths were used as tracers either carrier-free or with <1 g/l. of the corresponding natural isotopes as carriers. Y^{91}, Ce^{144}, Pm^{147} and Eu^{152} (with some Eu^{154}) were supplied by the Radiochemical Centre, Amersham. La^{140} was obtained by irradiation of the oxide and Nd^{147} by irradiation of the nitrate. Ce^{141} and Pr^{143} were obtained from ceric oxide irradiated in BEPO for 7 days and cooled for about 20 days to allow complete decay of Ce^{143} to Pr^{143}. The two elements were separated by means of a ceric iodate precipitation, purified by further precipitation cycles, and tested for radiochemical purity by means of absorption curves.

Y^{91}, La^{140}, Ce^{141}, Ce^{144}, Pr^{143}, and Pm^{147} were β-counted, Ce^{144} after allowing samples to stand for at least 2 hours to enable Pr^{144} to reach its equilibrium value. In order not to have too much material on the counting trays in the experiments with high concentrations of nitrates, aliquots from both the organic and aqueous phase were in such cases converted to their oxalates by coprecipitation with a standard quantity of calcium, and the oxalates, after being filtered, washed, and dried, were mounted for counting. The appropriate allowance (usually 2–3%) for self-absorption by the oxalate present was estimated from blank experiments with known quantities of the lanthanides. Nd^{147} and $Eu^{152+154}$ in both organic and aqueous phases were analysed by evaporating aliquots to dryness and γ-counting.

The diluents, "odourless" kerosene and xylene, were not specially purified. The TBP concentrations chiefly employed, 19%, 48%, 50%, and 100% v/v, correspond to 0·69, 1·76, 1·83, and 3·66 M respectively; after equilibration with an aqueous phase, the concentrations are, of course, rather lower owing to passage of water, nitric acid, etc., into the organic phase. In all cases, the cerium was in the trivalent state. All the experiments in Tables 1 and 2, except those for europium at 48% TBP, were carried out in a thermostat at 25°C, but the remainder were at room temperature, 20–23°C.

RESULTS AND DISCUSSION

Effect of varying the TBP concentration

Our partition results for yttrium and cerium at low TBP concentrations are plotted logarithmically in Fig. 1. The best lines through the points are in all cases of slope 2·7, and in our view they almost certainly imply a limiting cube law, and hence the formation of tri-solvates, $Y(NO)_3 \cdot 3TBP$ and $Ce(NO_3)_3 \cdot 3TBP$; some confirmation of the

[13] K. ALCOCK, F. C. BEDFORD, W. H. HARDWICK, and H. A. C. MCKAY *J. inorg. nucl. Chem.* **4**, 100 (1957).

latter formula is given by the composition of a saturated solution of cerium(III) nitrate in TBP.[14] Moreover, there is good evidence that the analogous elements, thulium and americium, form corresponding compounds.

At higher TBP concentrations there is generally a tendency towards a law of lower power than the third. This tendency is more marked at the lower acidities. For

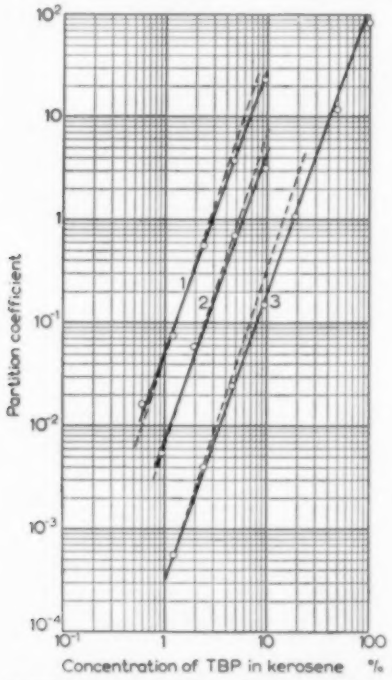

FIG. 1.—The partition coefficient as a function of TBP concentration.
Curve 1—D_Y from 5·2 M HNO_3, 0·8 M $NaNO_3$
2—D_{Ce} from 0·005 M HNO_3, 4·18 M $Ca(NO_3)_2$
3—D_Y from 13·5 M HNO_3.
Curve 1 has been displaced upwards by a factor of 10.
——— Lines of slope 2·7
– – – Lines of slope 3·0

example, our yttrium results in Fig. 2 for 19, 48, and 100% TBP in kerosene give a roughly 1·5-power law at 1 M HNO_3, a square law at 4 M HNO_3 and a cube law at 10 M HNO_3. Similarly, PEPPARD, FARIS, GRAY, and MASON[2] found an approximately square law for scandium, yttrium, and promethium at 1 M HNO_3, but a cube law at 4 and 11·5 M HNO_3 over the range 10–100% TBP in dibutyl ether. At 0·1 M HNO_3 in presence of 5 and 7 M NH_4NO_3, CUNINGHAME, SCARGILL, and WILLIS[10] found an approximately square-law dependence for praseodymium and neodymium for 30–100% TBP in kerosene. It should not be inferred from such results that the tri-solvates give place to lower solvates at the higher TBP concentrations; this would be contrary to the law of mass action. Rather must the deviations from limiting cube law be ascribed to deviations from ideality.[15]

[14] T. V. HEALY and H. A. C. MCKAY *Trans. Faraday Soc.* **52**, 633 (1956); *Rec. trav. chim.* **75**, 730 (1956).
[15] H. A. C. MCKAY To be published.

TABLE 1

Rare earth	TBP conc. (kerosene diluent)	HNO_3 conc. (aq)	Partition coefficient (org/aq)
Yttrium	19% v/v	0·48 M	0·0024
		0·90	0·0044
		2·26	0·0141
		3·68	0·0196
		4·62	0·020
		6·13	0·0162
		7·72	0·0185
		9·65	0·035
		12·1	0·22
		13·5	1·05
Yttrium	48%	0·42	0·0088
		0·50	0·013
		1·29	0·033
		1·95	0·048
		3·23	0·082
		3·70	0·101
		5·78	0·120
		7·07	0·148
		9·32	0·40
		11·2	1·40
		12·5	4·7*
			4·6*
			4·8*
Yttrium	100%	0·71	0·044
		1·52	0·100
		3·23	0·27
		4·84	0·64
		6·55	1·10
		7·14	1·38
		7·83	2·2
		9·10	3·6
		10·4	9·0
		10·9	13·8
		11·9	25
		12·2	32
		13·1	62
		13·8	113
		14·6	198
		15·0	220
Lanthanum	48%	5·22	0·0189
		6·88	0·0109
		10·8	0·0085
		12·7	0·0135
Lanthanum	100%	0·63	0·074
		1·21	0·108
		2·15	0·123
		3·17	0·124
		4·27	0·102
		6·10	0·076
		8·05	0·057
		10·2	0·060
		12·1	0·088
Lanthanum	100%	13·8 M	0·142
		15·0	0·22
Cerium(III)	48%	0·40	0·0186
		1·12	0·050
		1·50	0·057
		2·70	0·056
		3·98	0·040
		5·28	0·025
		7·06	0·0155
		9·30	0·0160
		11·2	0·023
		13·0	0·039
Cerium(III)	100%	0·27	0·028
		0·72	0·099
		0·98	0·123
		1·82	0·168
		2·38	0·172
		3·64	0·169
		5·20	0·133
		6·00	0·110
		6·85	0·098
		8·15	0·090
		8·95	0·096
		9·88	0·108
		11·3	0·133
		12·0	0·137
		12·9	0·195
		13·9	0·28
		14·5	0·36
		15·0	0·42
Promethium	48%	0·47	0·027
		0·83	0·051
		1·62	0·094
		2·57	0·116
		3·53	0·108
		5·85	0·068
		6·94	0·062
		7·46	0·056
		9·51	0·077
		11·2	0·146
		12·8	0·29
Europium	48%	0·05	0·0027
		1·00	0·074
		2·00	0·136
		3·00	0·160
		4·00	0·164
		5·00	0·156
		7·00	0·118
		8·00	0·144
		9·00	0·146
		10·0	0·191
		12·0	0·47

*Repeat experiments

TABLE 1—*continued*

Rare earth	TBP conc. (kerosene diluent)	HNO_3 conc. (aq)	Partition coefficient (org/aq)	Rare earth	TBP conc. (kerosene diluent)	HNO_3 conc. (aq)	Partition coefficient (org/aq)
		0·64 M	0·105			8·54 M	0·72
		1·67	0·30			8·92	0·76
		2·38	0·39			9·35	0·89
		3·76	0·49			10·1	1·24
		5·38	0·53			10·4	1·26
Europium	100%	6·11	0·54	Europium	100%	11·2	1·80
		6·30	0·54			11·6	2·2
		7·27	0·59			12·5	3·4
		7·22	0·58 (?)			14·6	9·7
		8·46	0·73			16·0	19·9
						18·7	64

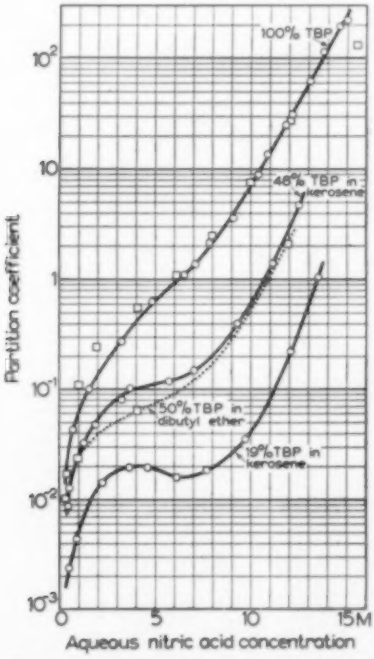

FIG 2.—The partition coefficient of yttrium nitrate.
○ Our data
□ PEPPARD, FARIS, GRAY, and MASON[2]

Extraction from nitric acid solutions

Our results are given in Table 1, and plotted in Figs. 2–4 along with comparable results by other authors. The latter are subject to the following comments:

(1) PEPPARD, FARIS, GRAY, and MASON'S[2] and PEPPARD, GRAY, and MARKUS'S[3] results are directly comparable with ours, except for their use of dibutyl ether as diluent. This must affect the results (except, of course, with 100% TBP), because dibutyl ether dissolves quite large amounts of nitric acid.

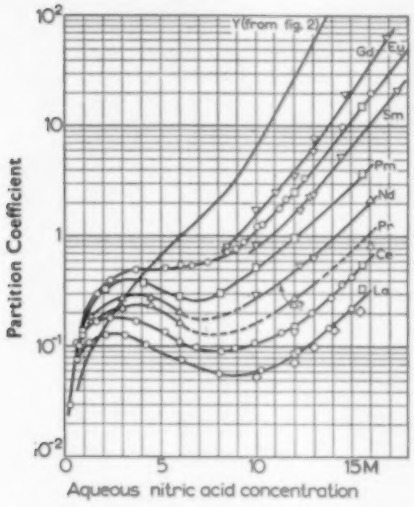

FIG. 3.—The partition coefficients of the lower lanthanide nitrates: 100% TBP.
○ Our data
△ CUNINGHAME, SCARGILL, and WILLIS[10]
□ PEPPARD, FARIS, GRAY, and MASON[2]; PEPPARD, GRAY, and MARKUS[3]
▽ TOPP and WEAVER[4–7]
◊ SUTTLE and STAMPFER[8]

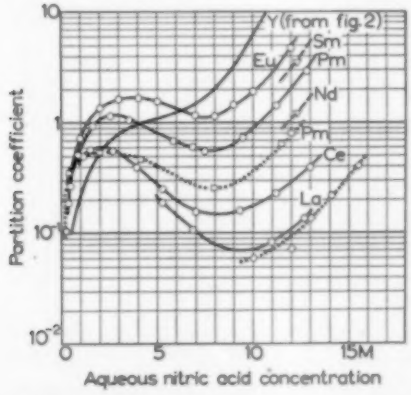

FIG. 4.—The partition coefficients of the lower lanthanide nitrates: 48% TBP in diluent (50% for PEPPARD *et al.*'s results).
○ Our data (diluent: kerosene)
□ PEPPARD, FARIS, GRAY, and MASON[2] (diluent: dibutyl ether)
▽ TOPP[4] (diluent: Varsol)
◊ SUTTLE and STAMPFER[8] (diluent: *n*-hexane)

(2) The Oak Ridge[4–7] results were generally obtained gravimetrically at a series of macro rare-earth concentrations. In extrapolating to trace concentration, it is necessary to ignore the anomalously high partition coefficients usually quoted for the lowest concentrations studied (where the analytical errors are presumably greatest). This procedure leads to figures consistent with those obtained with radioactive tracers. The two points in Fig. 4 necessitated a further extrapolation, since the TBP dilution data only covered the range 60–100% TBP in Varsol (a hydrocarbon diluent).

(3) The points ascribed to SUTTLE and STAMPFER[8] in Fig. 4 involved a similar extrapolation from the range 60–100% TBP in *n*-hexane.

(4) CUNINGHAME, SCARGILL, and WILLIS's[10] results were mainly obtained by gravimetric analysis at a low rare-earth concentration (0·4 g/l. initially), and are of limited accuracy.

BLACKMORE, BEARSE, and CALKINS' results[11] with 50% TBP in Sohio Solvent (another hydrocarbon diluent) have not been plotted, partly because they used macro rare-earth concentrations, but their data provide general confirmation of the curves in Fig. 4.

The shapes of the curves in Figs. 2–4 will be discussed in detail in another paper.[15] Briefly, the factors operating are:

(1) Salting-out from the aqueous phase by the nitrate ion.
(2) Formation of nitrate complexes.
(3) Nitric acid competition for the available TBP.
(4) Activity coefficient effects.

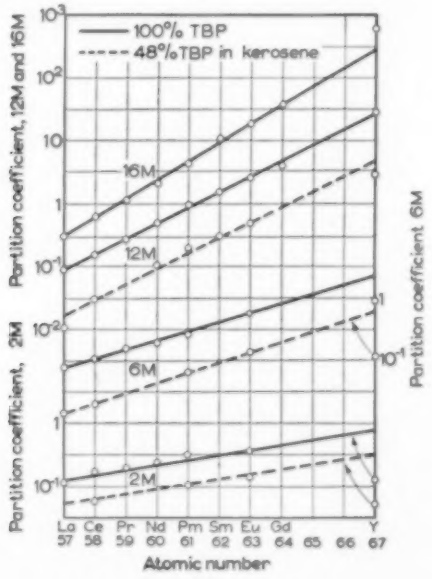

FIG. 5.

(1) accounts for the initial steep rise in the curves, at low acidities, while (2) and (3) provide a check on this rise at rather higher acidities, and often cause the partition coefficient to pass through a maximum. The further steep rise frequently observed at very high acidities (say >10 M) has not been properly explained, but may be due to (4).

The partition coefficient curves for the series of elements from lanthanum to gadolinium form a regularly spaced family. The family is characterized by a relation of the form of equation (1), as discussed in the first part of this paper. This is illustrated in Fig. 5. The logarithmic relation probably does not hold perfectly, but some of the deviations in Fig. 5 may be due to uncertainties in the experimental results.

Separation factors. The important quantity S, the separation factor for an adjacent pair of elements, may be obtained from the partition data for any pair of elements by taking the (Z_1-Z_2)th root of the ratio of partition coefficients (Z = atomic number). It may, of course, also be obtained from the slopes of the lines in Fig. 5, and if equation (1) held exactly, the two results would agree. The most reliable values of S can

probably be obtained from our cerium and europium data, as has been done in Fig. 6. Rather different curves are obtained with 48% and 100% TBP.

The principal feature of Fig. 6 is a steady rise in S from an extrapolated value of just over unity at zero acidity to nearly 2·0 at 16 M. The values of S at 12 and 15·6 M are rather larger than those given by PEPPARD, FARIS, GRAY, and MASON.[2] The high separation factors found at high acidities have been exploited at Oak Ridge for the separation of rare earths on a kilogram scale.

The position of yttrium. The behaviour of yttrium in relation to the lanthanides is of interest. This element is often regarded as a pseudo-lanthanide of atomic number *c.* 67, a position which accords with its Zachariasen ionic radius. PEPPARD,

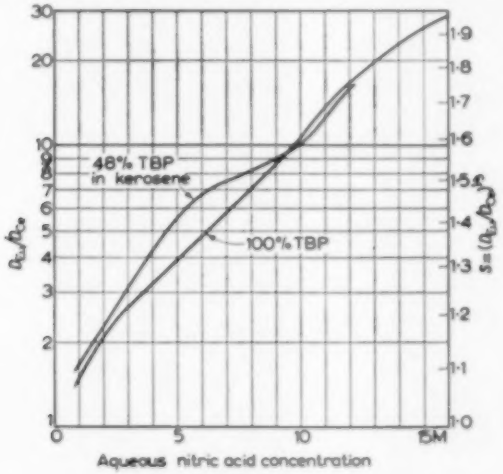

FIG. 6.—Separation factors.

FARIS, GRAY, and Mason[2] have pointed out that the TBP partition data at high acidities fit in fairly well with this idea, as can be seen from Fig. 5. At low acidities, however, yttrium behaves quite differently, becoming less extractable by nearly an order of magnitude than might have been expected. This will be discussed further in a later paper in this series, which deals with the higher lanthanides.

Extraction in presence of other nitrates

CUNINGHAME, SCARGILL, and WILLIS[10] have shown that praseodymium and neodymium extract much more readily from aqueous ammonium nitrate containing a little nitric acid, than from pure nitric acid of similar concentration. SUTTLE and POSKANZER[9] have made analogous observations with lanthanum, using calcium nitrate as the salting-out agent. In Table 2 we present some new results with cerium extracted from 6 M (HNO_3 + $NaNO_3$), illustrating the same point. The effect is not confined to the rare earths: it also occurs with thorium[16] and plutonium(IV).[17]

The results show that the partition coefficient can increase by several orders of magnitude when nitric acid in the aqueous phase is replaced by another nitrate at

[16] D. SCARGILL, quoted by H. A. C. MCKAY *Int. Conf. on the Peaceful Uses of Atomic Energy, Geneva* P/441. Vol. 7. p. 314. (1955).
[17] G. F. BEST, H. A. C. MCKAY, and P. R. WOODGATE *J. inorg. nucl. chem.* **4**, 315 (1957).

constant (stoichiometric) nitrate concentration. The effect becomes more marked as the nitrate concentration increases, at least up to 6–7 M. Moreover, it is in the last stages of replacement, when the nitric acid concentration is quite small, that the greatest rate of increase of extraction is observed.

TABLE 2.—48% TBP IN KEROSENE

HNO_3 conc. (aq)	4·00	1·50	0·50	0·20	0·05	0·005 M
$NaNO_3$ conc. (aq)	2·00	4·50	5·50	5·80	5·95	6·00 M
D_{Ce}	0·030	0·113	0·56	1·90	8·6	17·6

An explanation of the phenomenon can readily be given in terms of the factors listed earlier. Removal of nitric acid from the system means that less of the TBP is combined with the acid, i.e. more of the TBP is free; whilst the presence of an in-extractable nitrate maintains the salting-out effect of the nitrate ion. The nitric acid partition data in Table 4 enable us indeed to make a calculation showing that the rare-earth partition coefficients are roughly proportional to the cube of the concentration of free TBP; this is the power we should expect if tri-solvates $M(NO_3)_3 \cdot 3TBP$ are formed. The calculation emphasises the importance of reducing the aqueous acidity to a low value in order to obtain efficient utilization of the TBP.

TABLE 3.—50% TBP IN XYLENE

HNO_3 conc. (aq)	1·00	0·50	0·10	0·01 M	0·50 M	
Metal nitrate (aq)	———	6·00 M	$NaNO_3$	———	1·00 M	$Al(NO_3)_3$
HNO_3 conc. (org)	1·15	0·96	0·46	0·09 M	—	
Free TBP conc. (org)*	0·59	0·80	1·33	1·73 M	—	
D_{Ce}	0·16	0·45	3·4	8·5	—	
D_{Pr}	0·20	0·71	4·0	11·1	1·29	
D_{Nd}	0·35	1·0	5·7	12·6	1·75	
D_{Pr}/D_{Ce}	1·2	1·6	1·2	1·3	—	
D_{Nd}/D_{Pr}	1·8	1·4	1·4	1·2	1·4	
D_{Nd}/D_{Ce}	2·2	2·2	1·7	1·5	—	

* Assuming that all the acid in the organic phase forms a 1:1-compound with TBP.

Separation factors. Earlier work, e.g. that of CUNINGHAME, SCARGILL, and WILLIS,[10] indicates that good separation factors as well as high extraction can be obtained by working at low acidity but high nitrate concentration. Moreover, BOCHINSKI, SMUTZ, and SPEDDING[12] have used such conditions for the practical separation of the rare earths, utilizing the rare-earth nitrates themselves to obtain a high nitrate concentration. (One of their graphs, indeed, seems to indicate separation factors of 10 or more, but we think that a decimal point has been omitted and that their true *S*-value was about 1·4).

The results of a further study of the separation factors are shown in Table 3. The figures are somewhat scattered, but they indicate an *S*-value of about 1·4 for 6 M $NaNO_3$ plus small amounts of nitric acid; there is also possibly a trend towards

increasing separation factors as the acidity is increased. It is interesting to note, too, that 1 M $Al(NO_3)_3$ is apparently about as effective as 6 M $NaNO_3$ as regards both extraction and separation of the lanthanides. An isolated result with europium ($D_{Eu} = 67$ for 48% TBP in kerosene, and a 6 M $NaNO_3$, 0·05 M HNO_3 aqueous phase) yields a D_{Eu}/D_{Ce} ratio of 7·8, corresponding to $S = 1·5$.

Extraction in presence of complexing agents

One or two experiments have been carried out in the presence of lactic acid (Table 4). It will be seen that this reagent holds the rare earths back in the aqueous phase, and yields very poor separation factors. Addition of TTA (thenoyltrifluor-

TABLE 4.—50% TBP IN XYLENE

Aqueous phase: 6 M $NaNO_3$, 0·5 M lactic acid

pH (aq)*	2·0	3·5	2·0	3·5
TTA conc. (org)	Nil	Nil	0·20	0·20 M
D_{Ce}	0·71	0·010	19	>300
D_{Pr}	—	0·010	—	>300
D_{Nd}	0·68	0·011	21	>300

* Adjusted by adding ammonia.

acetone) to the system results in high extraction again, but the separation factors still seem poor. On the other hand, CUNINGHAME, SCARGILL, and WILLIS[10] have shown that good separation factors as well as high extraction are obtained with TTA-TBP mixtures in the absence of lactate.

Survey of separation factors

Typical values of S obtained under a variety of conditions are assembled in Table 5. These show that very high acidities probably yield the best separations,

TABLE 5

Aqueous phase	Organic phase*	Separation factor, S
Infinite dilution (extrapolated)	100% TBP	1·03
6 M HNO_3	48% TBP in kerosene	1·5
	100% TBP	1·4
12·3 M HNO_3	60–100% TBP in Varsol	1·7[4]
15·6 M HNO_3	100% TBP	2·0
6 M $NaNO_3$, 0·05 M HNO_3	48% TBP in kerosene	1·5
5–7 M NH_4NO_3, 0·1 M HNO_3	100% TBP	1·5[10]
1 M $Al(NO_3)_3$, 0·5 M HNO_3	50% TBP in xylene	1·4
6 M $NaNO_3$, 0·5 M lactic acid, pH 2	50% TBP in xylene	1·0
6 M $NaNO_3$, 0·5 M lactic acid, pH 2	50% TBP in xylene, 0·2 M TTA	1·05
1 M NH_4NO_3, pH 3·55	30% TBP in kerosene, 0·2 M TTA	2·4[10]

* The separation factors do not usually vary much with the dilution of the TBP.

though the device of using TTA-TBP mixtures deserves further study. Good separations can also be obtained at low acidities combined with high nitrate concentrations.

Our thanks are due to E. JACKSON for some of the europium results given in this paper.

Many of the results quoted here appeared originally in A.E.R.E. C/R 1514 (1954) by MCKAY, ALCOCK, and SCARGILL. The results quoted there for cerium(IV) nitrate are, however, erroneous.

Note added in proof. E. JACKSON has recently obtained the following results with europium at 15·6 M HNO_3 and varying TBP concentration:

TBP conc.	1%	2%	3%	4%	5% in kerosene
D_{Eu}	0·00029	0·0024	0·0076	0·0174	0·032 0·032

The best line through these points is of slope 3·0, indicating the formation of $Eu(NO_3)_3 \cdot 3TBP$.

J. Inorg. Nucl. Chem., 1957, Vol. 4, pp. 315 to 320. Pergamon Press Ltd., London

TRI-*n*-BUTYL PHOSPHATE AS AN EXTRACTING SOLVENT FOR INORGANIC NITRATES—III

THE PLUTONIUM NITRATES

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(*Received* 13 *December* 1956)

Abstract—Plutonium(III) nitrate is relatively inextractable by tri-*n*-butyl phosphate (TBP), but plutonium(IV) and plutonyl nitrates are freely extractable. Plutonyl nitrate is, however, less extractable than uranyl nitrate by a factor of about 10.

Experiments in which the TBP concentration was varied indicated the formation of $Pu(NO_3)_4 \cdot 2TBP$ and $PuO_2(NO_3)_2 \cdot 2TBP$.

In the case of plutonium(IV) nitrate it was shown that the temperature coefficient of extraction is small, that salting-out by sodium nitrate causes a striking increase in extraction, and that uranyl nitrate depresses the extraction. Increase in the plutonium(IV) nitrate concentration may either raise or lower the partition coefficient according to the conditions.

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TRI-*n*-BUTYL phosphate (TBP) is a good solvent for the extraction of plutonium from nitrate solutions. It was, for example, utilized in the isolation of plutonium from natural sources.[1] The tetra- and hexavalent states are very readily extracted, but trivalent plutonium, like the trivalent rare earths,[2] is relatively weakly extracted under most conditions. Plutonium can therefore be rendered extractable or inextractable by oxidation or reduction.

EXPERIMENTAL

The general techniques used were described in the first paper in this series.[3]

The plutonium was available initially in the tetravalent state in 6 M HNO_3. Plutonium(III) was prepared when required by dilution and addition of ferrous sulphamate and hydroxylamine as reductants; the latter reagent served to maintain a high Fe(II) : Fe(III) ratio, and hence to ensure complete reduction of the plutonium. Plutonium(VI) was prepared by anodic oxidation, but no steps were taken to remove residual plutonium(IV); this we now recognize as a blemish on our work, though we do not think it was of much effect numerically.

When the partition coefficients were fairly high, they were measured by a back-extraction technique. The plutonium was extracted into an organic phase, and this was then equilibrated with two successive portions of aqueous phase. This procedure should have eliminated traces of plutonium(III) in plutonium(IV) or (VI) partitions, and also traces of Am^{241} which might have grown from Pu^{241}; the agreement between the two successive measurements indicated whether the procedure had been successful. When the partition coefficients were low, forward partitions were used; two successive measurements again afforded a check on the presence of impurities, including especially higher valency states contaminating plutonium(III). Results for successive partitions seldom differed in fact by more than 2%; the results for plutonium(VI) showed the largest discrepancies, probably owing to the presence of plutonium(IV).

In most of the work the plutonium was used at a concentration of *c.* 0·1 g/l (0·0004 M). This is effectively a trace concentration, i.e. it is negligible in comparison with the concentrations of the major

[1] D. F. PEPPARD, M. H. STUDIER, M. V. GERGEL, G. W. MASON, J. C. SULLIVAN, and J. F. MECH *J. Amer. chem. Soc.* **73**, 2529, 3278 (1951).
[2] D. SCARGILL, K. ALCOCK, J. M. FLETCHER, E. HESFORD, and H. A. C. MCKAY *J. inorg. nucl. Chem.* **4**, 304 (1957).
[3] K. ALCOCK, F. C. BEDFORD, W. H. HARDWICK, and H. A. C. MCKAY *J. inorg. nucl. Chem.* **4**, 100 (1957).

components (nitric acid, TBP, etc.). Moreover, it is low enough to ensure that plutonium(IV) will not disproportionate appreciably during the time of the experiment. According to HALL's data,[4] less than 1% disproportionation will occur in 10 min at 25°C (a) with 2 g/l of plutonium at acidities above 0·25 M HNO_3, and (b) with 5 g/l at acidities above 0·40 M HNO_3. Hence even our experiments at higher plutonium concentrations should be unaffected by disproportionation.

Some of the partitions were carried out at room temperature (20–23°C), and some in a thermostat (25°C or 40°C). The TBP was diluted throughout with "odourless" kerosene.

Plutonium was determined by α-counting, and acidities by titration with alkali. In the series at higher plutonium concentrations, the plutonium was precipitated as ferrocyanide prior to alkali titration of the aqueous phase.[5] The general level of reproducibility of the final results was ±10%.

Such other data as are available for comparison are in general agreement with ours, but very little numerical information has appeared in the open literature.

RESULTS AND DISCUSSION

Plutonium(III) nitrate

Plutonium(III) nitrate only extracts weakly into 19% v/v (0·69 M) TBP in kerosene: These results, which are plotted in Fig. 1, are in general accord with those for other

TABLE 1

HNO_3 conc (aq.)	0·20	0·65	1·20	2·0	3·0	4·0	5·0 M
Partition coeff. (org./aq.)	0·0027	0·0089	0·0157	0·0167	0·0161	0·0126	0·0116

trivalent lanthanides[2] and actinides. They imply, of course, that nearly all the plutonium(III) will be left behind in the aqueous phase in an extraction under the conditions in question.

Plutonium(IV) nitrate

Extraction from nitric acid solutions—Plutonium(IV) nitrate is highly extractable by 19% TBP in kerosene, maximum extraction from nitric acid solutions being observed at *c.* 7 M HNO_3. Our results are given in Table 2. The two series at 20–23°C

TABLE 2

HNO_3 conc (aq.)	0·15	0·21	0·44	0·52	0·62	0·82	0·84	0·86	0·91	1·28	1·41	2·65 M
Partition coeff. 25°C	0·114	0·204	0·39	0·41	0·72	1·01	1·14	1·20	1·30	2·20	2·37	5·7
(org./aq.) 40°C	—	0·166	0·33	—	—	—	1·01	1·19	—	—	2·54	5·9

HNO_3 conc (aq.)	2·2	3·0	4·0	5·0	6·0	7·0	8·0	10·0	11·5	13·5 M
Partition coeff. (org./aq) 20–23°C	3·9	6·8	11·5	16·6	19·6	20·2	18·2	13·0	6·1	3·0

and 25°C fit reasonably well together, as Fig. 1 shows; the 25°C data represent later and more careful work. The 40°C measurements were carried out on the same solutions as the 25°C measurements in order to obtain good comparisons: equilibrium was established at 25°C, samples were taken for analysis, the temperature was raised to 40°C, equilibrium was re-established, and further samples were taken for analysis.

[4] G. R. HALL, private communication.
[5] B. A. J. LISTER, I. L. JENKINS, and N. J. KEEN *A.E.R.E. C/M* 165 (1953).

The temperature coefficient is clearly low, and corresponds to a heat of transference of plutonium(IV) nitrate between phases of less than 2000 cal/mole.

Further measurements were made at 20–23°C at lower TBP concentrations:

TABLE 3

HNO_3 conc (aq.)	Partition coeff. (org./aq.)		
	1·9%	4·8%	9·5% TBP in kerosene
1·0 M	0·015	0·13	0·43
7·0	0·50	2·4	8·7
11·5	0·13	0·65	2·3

These, in combination with data from Table 2 (interpolated in one instance), indicate that, as a limiting law at low TBP concentrations, the partition coefficient depends on the square of the TBP concentration (see Fig. 2). This implies the formation of a disolvate $Pu(NO_3)_4 \cdot 2TBP$, analogous to the corresponding zirconium compound.[3]

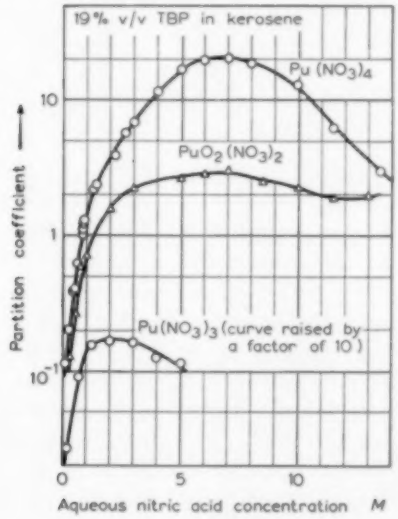

FIG. 1

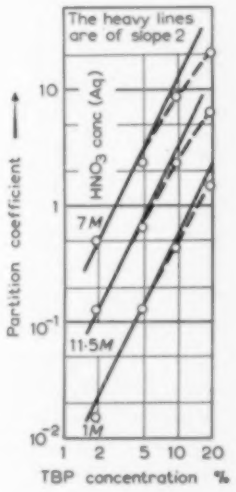

FIG. 2

Spectroscopic evidence supports the postulate that there are four nitrate groups in the complex[6].

The deviations from the square law in Fig. 2 (due presumably to nonideality) are appreciable but hardly sufficient to make us doubt that it is the true limiting law. They are, moreover, similar at all acidities. This means that the curve in Fig. 1 retains its shape as the TBP concentration is varied; it merely suffers a vertical displacement.

Another series of measurements has been carried out at 25°C at rather higher plutonium concentrations, with the results given in Table 4. Fig. 3 gives smoothed curves based on these data. The check indicated by the footnote to the table shows that disproportionation did not vitiate the results, even at the lowest acidities.

Table 4.—19% v/v TBP in kerosene

HNO_3 conc (aq.)	Plutonium concentrations (g/l.)		Partition coefficient (org./aq.)
	Aqueous	Organic	
0·22 M	2·07	0·38	0·18
0·31	2·42	0·62	0·26
0·34	0·71	0·19	0·27
0·39	2·20*	0·76	0·37
0·43	6·22	2·96	0·48
0·50	5·39	3·86	0·71
0·55	1·18	0·72	0·61
0·63	2·18	1·50	0·69
0·65	4·28	3·05	0·71
0·70	4·26	4·00	0·94
0·85	1·50	1·80	1·20
0·89	2·68	3·39	1·27
0·90	7·16	8·35	1·47
1·15	3·64	6·07	1·67
1·32	4·97	8·40	1·69(?)
1·33	3·50	8·45	2·40
1·64	4·43	11·6	2·61

* Unchanged after 5 hr equilibration

The rise in the partition coefficient with plutonium concentration at low acidities may be ascribed to increased salting-out, due to additional nitrate ion present in the aqueous phase. If there were no complications, the partition coefficient would be proportional to the fourth power of the nitrate ion concentration. On increasing the plutonium concentration from trace level to 4·8 g/l. (0·02 M), the partition coefficient would therefore increase by a factor of $(0{\cdot}58/0{\cdot}50)^4 = 1{\cdot}80$ at 0·5 M HNO_3 and $(1{\cdot}08/1{\cdot}00)^4 = 1{\cdot}40$ at 1·0 M HNO_3. The actual increases are by factors of 1·38 and 1·10 respectively. These are smaller than those just calculated, mainly on account of nitrate-complexing of Pu^{4+} ions in the aqueous phase; if, for example, we assume that all the plutonium is complexed as $PuNO_3^{3+}$ at 0·5 M HNO_3, then we should expect a factor of $(0{\cdot}56/0{\cdot}50)^3 = 1{\cdot}40$, which is very close to the experimental figure. At higher acidities, when most of the plutonium is in the organic phase, a further effect becomes important, namely (partial) plutonium saturation of the TBP, which reduces the partition coefficient. Our data suggest that the null region, where the partition coefficient is independent of plutonium concentration, is around 1·2 M HNO_3.

Beyond a certain plutonium concentration (*c.* 10 g/l.) the organic phase divides into two, a TBP-rich and a kerosene-rich fraction.[6]

Extraction in presence of sodium nitrate—There is a striking rise in the partition coefficient for plutonium(IV) when nitric acid in the aqueous phase is replaced, mole for mole, by sodium nitrate; similar results have been obtained for the rare earths[2] and thorium. Our results for plutonium are given in Fig. 4, and were obtained at 20–23°C. The true figures may be somewhat lower than our measurements indicate, as we may have underestimated the plutonium concentrations in the aqueous phase.

[6] T. V. Healy and H. A. C. McKay *Trans. Faraday Soc.* **52**, 633 (1956).

GOULDEN, DURHAM, and CORRIVEAN's results[7] on the extraction of plutonium in presence of 0·45 M $Al(NO_3)_3$ show that aluminium nitrate is a more powerful salting-out agent than sodium nitrate. 0·45 M $Al(NO_3)_3$ is about as effective as 2 M $NaNO_3$ at 1–2 M HNO_3, and about as effective as 3 M $NaNO_3$ at 4–5 M HNO_3. A similar difference between the two nitrates has been noted in relation to the lanthanides.[2]

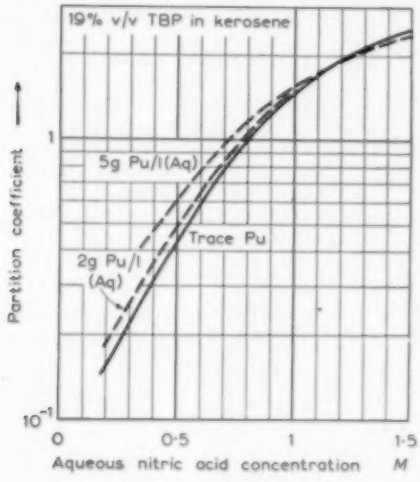

FIG. 3

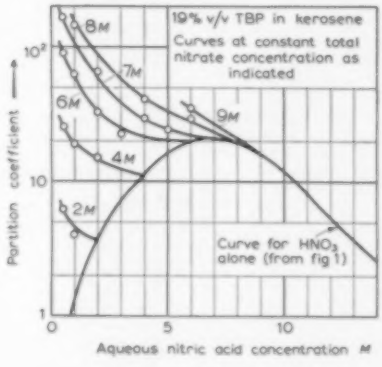

FIG. 4

Extraction in presence of uranyl nitrate—Uranyl nitrate depresses the extraction of plutonium(IV), just as it does that of zirconium.[3] A typical series of results at 25°C is given in Table 5. The figures in brackets refer to partition at zero or trace uranyl

TABLE 5.—19% v/v TBP IN KEROSENE

Concentrations			Partition coefficients (org./aq.)	
HNO_3 (aq.)	$UO_2(NO_3)_2$ (aq.)	$UO_2(NO_3)_2$ (org.)	Pu(IV)	UO_2
0·20 M	0·024 M	0·011 M	0·13 (0·16)	0·48 (0·5)
0·50	0·024	0·039	0·43 (0·47)	1·6 (1·6)
0·70	0·024	0·063	0·62 (0·83)	2·7 (3·0)
1·00	0·027	0·087	0·90 (1·5)	3·2 (4·2)
1·50	0·028	0·131	1·18 (2·6)	4·8 (7·4)

nitrate concentration; for plutonium(IV) they have been taken from Fig. 1, and for uranyl nitrate from unpublished results by G. F. BEST.

The main reason for the lowering of the partition coefficients is loading of the organic phase with uranyl nitrate, so that there is less free TBP. This causes a parallel lowering of all partition coefficients, including that of uranyl nitrate itself, as the last two columns illustrate.

[7] P. D. GOULDEN, R. W. DURHAM, and V. CORRIVEAN *CRDC*-640 (1955).

Plutonyl nitrate

Our results for the distribution of traces of plutonyl nitrate in presence of nitric acid at 20–23°C for 19% TBP in kerosene are shown in Fig. 1. As has already been mentioned, we have reason to suspect the presence of a small proportion of plutonium (IV) nitrate in our material. 5% of plutonium(IV) would mean an overestimation of the partition coefficient of 9% at the maximum in the curve, with the backextraction procedure used, and rather less elsewhere. The true curve may therefore be a few per cent lower than that shown in Fig. 1.

We have also obtained some results at lower TBP concentrations; though rather erratic, they suggest a square-law dependence of partition coefficient on TBP concentration in the limit, and hence the formation of $PuO_2(NO_3)_2 \cdot 2TBP$, analogous to $UO_2(NO_3)_2 \cdot 2TBP$.

It is noteworthy that plutonyl nitrate is less extractable than uranyl nitrate by a factor of about 10. This is a reversal of the usual trend of increasing extractability with increasing atomic number in the lanthanide and actinide series.

The present paper is based on two A.E.R.E. reports, C/R 994 (1952) by McKay and Woodgate, and C/R 1116 (1953) by McKay and Best. The authors wish to thank Dr. J. M. Fletcher for his encouragement in carrying out this investigation.

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TRI-*n*-BUTYL PHOSPHATE AS AN EXTRACTING SOLVENT FOR INORGANIC NITRATES—IV

THORIUM NITRATE

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(*Received* 1 *March* 1957)

Abstract—Thorium nitrate is more readily extracted by tri-*n*-butyl phosphate (TBP) than are the rare earths, but it is less extractable than plutonium(IV) nitrate by a factor of about 10.

It extracts as a di-solvate, $Th(NO_3)_4 \cdot 2TBP$, according to solubility measurements and to partition data at varying TBP concentrations.

It extracts more readily from slightly acidified sodium nitrate than from nitric acid of similar concentration, but if the pH rises above about 3 the partition coefficient falls again owing to thorium hydrolysis.

THORIUM nitrate is quite strongly extracted by tri-*n*-butyl phosphate (TBP). The extraction is sufficiently good with fairly concentrated TBP (say 40 per cent in a diluent) for the separation of thorium from most of the fission products,[1] or from the rare earths in monazite.[2] On the other hand, with more dilute TBP (say 5 per cent) thorium itself becomes difficult to extract, whereas uranium is still quite extractable; this is made use of in isolating ^{233}U from irradiated thorium.[1]

EXPERIMENTAL

The general techniques used were described in Part I.[3]

Our earliest work on thorium employed ^{232}Th, the principal naturally-occurring isotope. This was determined colorimetrically by titration with fluoride, using Chromazural Blue (also called Solochrome Blue) as an indicator. The method was, however, scarcely sensitive enough at the low levels it was desired to study; indeed, it was necessary to work at a slightly higher level (*c.* 2 g/l. in the initial aqueous phase) than we would have chosen. Moreover, there were rather uncertain corrections for temperature and nitrate ion concentration.

Later, a small quantity of ^{234}Th (UX_1) was supplied by the Radiochemical Centre, Amersham. This was assayed by β-counting, using the 2·3 MeV β-particles of the ^{234}Pa (UX_2) daughter. The material had been obtained by washing out the residue from a cylinder in which uranium hexafluoride had been stored, but unfortunately no more ^{234}Th was forthcoming from this source.

Finally, some ^{230}Th (ionium) became available from one of the residues from the Springfields uranium plant.[4] It was admixed with much ^{232}Th (12 per cent ^{230}Th, 88 per cent ^{232}Th) but was nevertheless quite active enough for α-counting.

RESULTS AND DISCUSSION

Effect of Varying the TBP Concentration

Two series of results at varying TBP concentration but constant composition of aqueous phase are shown in Fig. 1. They were obtained at 25°C with the aid of ^{230}Th.

(1) H. A. C. MCKAY and J. M. FLETCHER *Progress in Nuclear Energy, Series* III. Vol. 1. p. 147. (1956).
(2) A. AUDSLEY, R. LIND, and P. G. ENGLAND Paper 20, *I.M.M. Symposium on the Extraction Metallurgy of Some of the Less Common Metals* (Mar. 1956). See also *TID*-3310 (1956), *Production of Thorium Metal* (a bibliography).
(3) K. ALCOCK, F. C. BEDFORD, W. H. HARDWICK, and H. A. C. MCKAY *J. inorg. nucl. Chem.* **4**, 100 (1957).
(4) D. J. CARSWELL, D. W. CLELLAND, and J. M. FLETCHER *J. inorg. nucl. Chem.* To be published.

The slopes of the best lines through the points are 2·4 and 2·0 respectively. As the latter refers to much lower TBP concentrations than the former, it seems reasonable to suppose that the limiting law at low TBP concentrations is a square law, implying the formation of $Th(NO_3)_4 \cdot 2TBP$, analogous to $Zr(NO_3)_4 \cdot 2TBP$ and $Pu(NO_3)_4 \cdot 2TBP$. HARDWICK, SWIFT, and TODD[5] have shown, moreover, that the composition of a saturated solution of thorium nitrate in TBP approaches that represented by $Th(NO_3)_4 \cdot 2TBP$ asymptotically as the temperature is raised.

PEPPARD, MASON, and MAIER[6] also report a square law for 25–100 per cent TBP in benzene at 1·9M HNO_3, but a cube law at 6·1M HNO_3, and a fourth-power law at

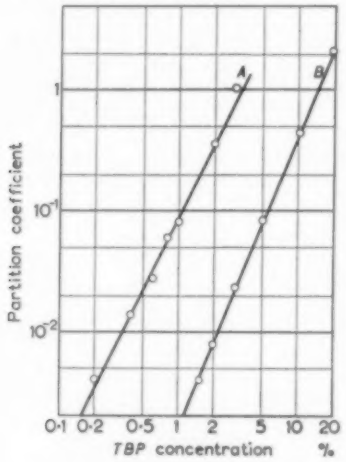

FIG. 1.
A. Aqueous phase: 0·1M HNO_3, 6M $NaNO_3$. Line of slope 2·0.
B. Aqueous phase: 5M HNO_3. Line of slope 2·4.

10·1M and 13·8M HNO_3. Our own results indicate a cube law at 10M HNO_3 for 19–100 per cent TBP in kerosene (though a square law at both 4·5M and 16M HNO_3). It is, however, no cause for surprise if the limiting law gives place to some other relationship at such high TBP concentrations. Moreover, benzene is by no means an inert diluent, since it dissolves appreciable amounts of nitric acid. It would be unwarrantable, therefore, to deduce the formation of a tri- or tetra-solvate from these results.

Other authors have, nevertheless, postulated such compounds. GERCKE[7] proposed a tri-solvate on the basis of not very accurate solubility studies, and calculated an equilibrium "constant" for its formation from his partition data; but the "constant" varied by a power of 10 from experiment to experiment and took no account of either nitrate complexing of thorium or activity coefficients. Oak Ridge papers at Geneva[8] referred to a tetra-solvate, but did not present the evidence for it. There seems, therefore, every reason at present to adhere to our conclusion that a di-solvate is formed.

[5] W. H. HARDWICK, R. TODD, and P. SWIFT *A.E.R.E. C/M* 152 (1955) quoted in ref. 10.
[6] D. F. PEPPARD, G. W. MASON, and J. L. MAIER *J. inorg. nucl. Chem.* **3**, 215 (1956).
[7] R. H. GERCKE *UCRL*–1493 (1951).
[8] A. T. GRESKY (P/540) and F. L. CULLER (P/822) *Peaceful Uses of Atomic Energy, Geneva* (1955).

Extraction from Nitric Acid Solutions

The results in Table 1 were obtained at 25°C, using ^{230}Th.

TABLE 1

(a) 19 per cent v/v (0·69M) TBP in kerosene

HNO_3 conc. (aq)	0·65	1·24	1·61	2·35	4·40	6·60	8·0	9·9	12·3	13·1	14·0	15·0M
Partition coeff. (org/aq)	0·156	0·50	0·78	1·39	2·09	2·16	1·97	2·08	3·3	4·0	5·8	9·1

(b) 48 per cent v/v (1·74M) TBP in kerosene

HNO_3 conc (aq)	0·41	0·87	2·09	4·18	6·89	8·2	10·0	12·2	13·0	13·9	15·4M
Partition coeff. (org/aq)	0·205	1·01	4·0	10·1	18·8	13·7	33	48	53	67	96

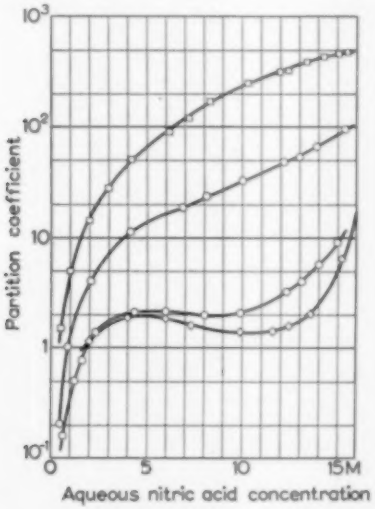

FIG 2.

○ Our data, 19 and 48 per cent TBP in kerosene.
□ PEPPARD, MASON, and MAIER,[6] 100 per cent TBP.
◇ PEPPARD, MASON, and MAIER,[6] 25 per cent TBP in benzene.

They are in general agreement with earlier but less accurate work using natural thorium ^{232}Th and ^{234}Th. In Fig. 2 they have been plotted along with PEPPARD, MASON, and MAIER's curves[6] for 25 per cent TBP in benzene and for 100 per cent TBP. As already mentioned, benzene is not strictly comparable with kerosene as a diluent, especially at high acidities.

Fig. 1 is reminiscent of the corresponding diagram for yttrium,[9] which also yields a continuously rising curve with 100 per cent TBP and one with a shallow maximum

[9] D. SCARGILL, K. ALCOCK, J. M. FLETCHER, E. HESFORD, and H. A. C. MCKAY *J. inorg. nucl. Chem.* **4**, 304 (1957).

and minimum with 19 per cent TBP in kerosene. Thorium is, however, considerably more extractable than the rare earths, though less extractable than plutonium(IV) by a factor of about 10.

Attention may be drawn to the fact that $Th(NO_3)_4 \cdot 2TBP$ has only a limited solubility in paraffinic hydrocarbons. Two organic phases, one TBP-rich and the other kerosene-rich, are thus often formed at macro concentrations of thorium.[10]

Extraction in Presence of Sodium Nitrate

Thorium nitrate is very much more extractable from slightly acidified sodium nitrate solution, than from nitric acid of similar concentration.[11] This is illustrated by the results at 20–23°C in Fig. 3, which may be compared with the very similar

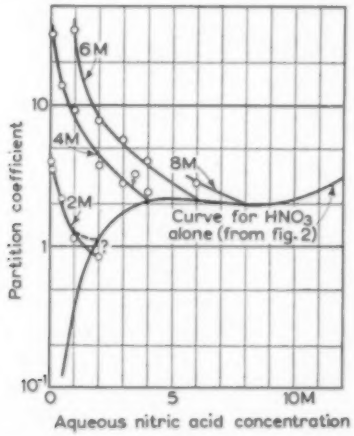

FIG. 3.
19 per cent v/v TBP in kerosene. Curves at constant total nitrate concentrations as indicated.

diagram already published for plutonium(IV) nitrate.[12] These experiments used natural ^{232}Th, for which the analytical methods available are of limited accuracy; this accounts for the slight discrepancies with the results in Fig. 1, and also renders it unwise to make detailed comparisons with the results for plutonium(IV) nitrate.

TABLE 2

$NaNO_3$ conc. (aq)	2·0	4·0	6·0M
Partition coeff. (org/aq)	1·1	3·2	8

Presumably the explanation of the rise in the partition coefficient as sodium nitrate replaces nitric acid is the same as that already advanced in other instances,[9,12] viz. a reduction in nitric acid competition for the available TBP.

If no acid at all is added to the system, relatively low partition coefficients are again observed (Table 2). This is presumably due to hydrolysis of the thorium, yielding

[10] T. V. HEALY and H. A. C. MCKAY *Trans. Faraday Soc.* **52**, 633 (1956).
[11] First observed by T. V. HEALY and A. W. GARDNER and quoted in *A.E.R.E. C/R* 986 (1952).
[12] G. F. BEST, H. A. C. MCKAY, and P. R. WOODGATE *J. inorg. nucl. Chem.* **4**, 315 (1957).

inextractable species. The fact that as little as 0·01M nitric acid was sufficient to prevent any fall in the thorium partition coefficient is in accord with the observation that, at low thorium concentrations, thorium hydrolysis first becomes appreciable when the pH exceeds 3.[13]

Acknowledgements—Our thanks are due to G. N. NAISH and V. J. WHEELER for preliminary work on the TBP extraction of thorium, which was reported in *A.E.R.E. C/R* 1168 (1953) by H. A. C. MCKAY, G. N. NAISH, and D. SCARGILL, and in P/441 of *Peaceful Uses of Atomic Energy, Geneva* (1955). This work is, however, superseded by the more accurate results using ^{230}Th reported in the present paper.

[13] K. A. KRAUS and R. W. HOLMBERG *J. phys. Chem.* **58**, 325 (1954); S. HIETANEN *Rec. trav. chim.* **75**, 711 (1956).

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J. Inorg. Nucl. Chem., 1957, Vol. 4, pp. 326 to 333. Pergamon Press Ltd., London

NONMONOTONIC ORDERING OF LANTHANIDES IN TRIBUTYL PHOSPHATE-NITRIC ACID EXTRACTION SYSTEMS*

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(*Received* 15 *February* 1957)

Abstract—The partition of tracer-level lanthanides, yttrium, and americium between various tri-*n*-butyl phosphate (TBP) phases and aqueous nitric acid phases has been studied radiometrically as a function of solvent concentration, nitric acid concentration, and Z.

In undiluted TBP systems, a plot of log K vs. Z approximates two straight lines joining at $Z = 64$. The line for the high-Z region has a positive slope somewhat less than that of the line for the low-Z region at 18·5 M HNO_3. This difference in slope becomes intensified as the concentration of nitric acid is lowered, the high-Z line ultimately acquiring a negative slope. The slope of the low-Z line remains positive throughout the region studied.

This general half-filled shell effect is also noted for systems involving diluted TBP.

It is postulated that the extracting species is $[M(TBP)_a(H_2O)_{(z-a)}](NO_3)_3$, in which a is a function of the nitric acid concentration and of Z.

In all of the systems studied, for plotting purposes yttrium may be assigned an "apparent Z" of 65–68. In the dilute nitric acid systems, the americium plot is nearly coincident with that for praseodymium.

IN THE initial investigations of the tri-*n*-butyl orthophosphate, $(n\text{-}C_4H_9O)_3PO$, symbolized as TBP, vs. nitric acid extraction system as a means of fractionation of trivalent lanthanides, it was reported by PEPPARD *et al.*[1] that in systems involving undiluted TBP a plot of log K vs. Z is essentially a straight line of positive slope in the high-acid range, whereas an inversion of certain members occurs as the concentration of nitric acid is lowered. Whether the monotonic variation holds throughout the entire 57–71 range in Z for high-acid concentration and the nature and extent of the inversion at lower-acid concentrations were not investigated in the previous study, due to lack of pertinent radioactive lanthanide nuclides of the required purity.

Following the acquisition of such nuclides, the investigation was extended, and the study presently reported treats these latter problems.

EXPERIMENTAL

Sources of materials. Tributyl phosphate was obtained from Commercial Solvents Corporation and treated as described below before use. Reagent-grade carbon tetrachloride and toluene were used as diluents as received. The beta-active nuclides Sr^{90}-Y^{90}, Ba^{140}-La^{140}, Ce^{144}-Pr^{144}, 2·6 y Pm^{147}, and (13,16) y Eu ^{152,154} were obtained from the Isotopes Division of the Oak Ridge National Laboratory. The 40·2h La^{140} was separated from its Ba^{140} parent (and the small accompanying contamination of Sr^{90} and Y^{90}) and the 64h Y^{90} from its Sr^{90} parent by solvent extraction processes.[2]

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.
[1] D. F. PEPPARD, J. P. FARIS, P. R. GRAY, and G. W. MASON *J. phys. Chem.* **57**, 294 (1953).
[2] D. F. PEPPARD, G. W. MASON, and S. W. MOLINE *J. inorg. nucl. Chem.* In press.

The 285-d Ce^{144} was oxidized to the tetravalent state and separated by a solvent extraction process[2] from traces of beta-active contaminants. The Pm and Eu tracers were further purified by a solvent extraction process[3] in which the conditions were so adjusted that approximately 10% yield, with concomitant high degree of purity, of product resulted. Beta-active 13·8d Pr^{143} was prepared by neutron irradiation of highly-purified gross cerium.[2] The beta-active nuclides, 72d Tb^{160}, 129d Tm^{170}, (32, 4·2)d $Yb^{169,175}$ and 6·8d Lu^{177} were obtained from D. C. STEWART of A.N.L., who prepared them by neutron irradiation of highly-purified lanthanides. These were all purified further by techniques similar to those used for the Pm and Eu tracers.[3] Alpha-active 470y Am^{241} was obtained from A.N.L. stocks and purified further by solvent extraction of Am(VI).[4]

Purification of TBP. The TBP, as received, was found to contain small quantities of butyl alcohol, dibutyl phosphoric acid, monobutyl phosphoric acid, and a component which was an extremely efficient extractant compared with pure TBP. This latter component was assumed to be a pyrophosphate ester. The TBP was stirred with an equal volume of 6 M HCl at 60°C for a 12 hr period to hydrolyse any pyrophosphate components. (This treatment also results in increasing the quantities of dibutyl phosphoric acid and monobutyl phosphoric acid and presumably results in the formation of some butyl alcohol and phosphoric acid.) The separated TBP phase was cooled to room temperature and scrubbed with two equal-volume portions of water (to remove most of the mineral acid), three equal-volume portions of 5% aqueous sodium carbonate (to remove the di-ester and the mono-ester), and three equal-volume portions of water. The resultant TBP phase was then slowly raised to a temperature of 30°C, under reduced pressure, to eliminate butyl alcohol and water.

Preparation of tracer solutions. In the early stages of this investigation it was found that, in certain instances, partial hydrolysis of the tracer-level nuclide had occurred, resulting in an error in the distribution ratio, the measured value being lower than the true value by a few per cent in the low-K region and by several hundred per cent in the high-K region. This source of error was eliminated by heating the tracer-nuclide in aqueous 8 M HNO_3 at 60°C for 24 hr, diluting the cooled solution to 2 M HNO_3, and storing the tracer in this form until ready for use.

Determination of distribution ratios. In the determination of the distribution ratio, K, of a specific nuclide, defined as the concentration of nuclide in the organic divided by the concentration of nuclide in the aqueous of two equilibrated sensibly-immiscible liquid phases, a portion of aqueous acid of the indicated concentration containing one or more radioactive nuclides was equilibrated against a portion of solvent which had previously been pre-equilibrated with respect to the corresponding barren aqueous acid. For example, a 1 ml portion of 10·1 M HNO_3 containing approximately 10^5 c/m each of beta-active Pr^{143} and alpha-active Am^{241} was equilibrated with a 1 ml portion of undiluted TBP which had previously been contacted with five successive equal-volume portions of barren 10·1 M HNO_3. (All solvent pre-equilibrations were made immediately prior to use to avoid any complications arising from solvent hydrolysis.) Aliquots of each phase were evaporated on 3 mil platinum discs $\frac{15}{16}$ in. in diameter, by means of induction heating, for beta and alpha counting. Beta counting was done by means of an end-window proportional counter, using

[3] D. F. PEPPARD, G. W. MASON, J. L. MAIER, and W. J. DRISCOLL. In press.
[4] D. F. PEPPARD, W. J. DRISCOLL, and G. W. MASON. To be submitted to *J. inorg. nucl. Chem.*

suitable absorber where needed. Alpha counting was done by means of an internal proportional counter.

In general, each of the entire series of nuclides was studied in the presence of a single specific nuclide considered to be the normalizing element. For example, in the 10·1 M HNO_3 *x* undiluted TBP system Am^{241} was used as the normalizing nuclide with all of the data normalized to the average value obtained for Am. A set of data were considered acceptable only if all Am values were within 10% of the average value. In instances in which Am^{241} was used as an internal normalizing nuclide, the beta activity was counted through 10 mg of aluminium absorber. (A correction of 13 c/m per 10^3 c/m of Am^{241} was still required.) In instances in which Pm^{147} was used as an internal normalizing standard, a great preponderance of Pm^{147} was used, so that only a small subtraction from the total measured activity was required in order to obtain that due to Pm.[147] The activity of the accompanying nuclide was obtained by using 40 mg of aluminium absorber to lower the Pm^{147} contribution to a sufficiently low value to permit valid correction.

Although it was established, in separate experiments with Pr^{143} and Tm,[170] that 30 sec mixing periods were sufficient to establish equilibrium in both the high-acid and low-acid studies, all data were obtained using 3 min mixing periods. The phases, in glass-stoppered 5 ml glass cylinders, were mixed by violent shaking, the two phases co-transferred to a centrifuge cone, the mixture centrifuged at full speed for a 1 min period in an International Clinical Centrifuge, Model CL, the lower phase transferred (by pipette) to a new centrifuge cone (leaving a small heel of lower phase to minimize the possibility of inclusion of traces of the upper phase), both phases centrifuged in their separate cones for a 1 min period, and aliquots of each phase then taken for analysis.

In several instances, the resulting pregnant organic extract was contacted with fresh barren aqueous acid and a redetermination of *K* made to establish the attainment of equilibrium and the absence of hydrolysis errors.

All data were obtained at $22 \pm 2°C$. The temperature effect within this range was shown to be within the error of the determination.

RESULTS AND CONCLUSIONS

In Fig. 1, the variation of log *K* with concentration of HNO_3 in the aqueous phase is shown for Eu(63) and Tb(65) and for Pr(59) and Tm(69). It may be noted that 63 and 65 are symmetrically located with respect to 64 as are 59 and 69 and that the 63 and 65 curves intersect at a point corresponding to approximately 2·9 M HNO_3 as do the 59 and 69 curves. Other examples of the same behaviour, not shown graphically, are the 57 and 71 pair and the 58 and 70 pair.

In Fig. 2, the variation of log *K* with concentration of HNO_3 in the aqueous phase is shown for a number of lanthanides, yttrium, and americium. The placement is arbitrary in order to avoid confusion, each of the curves being displaced upward one log unit with respect to the curve immediately below it with the exception of the curve for Am(95), which is placed at the very top for ease of comparison. On an absolute plot, the curve for Am is very nearly coincident with that for Pr in the region to the left of 8 M HNO_3, and at 18·5 M HNO_3 the value of the *K* for Am is only twice that of the *K* for Pr. It may be noted that on the basis of the shape of the curves yttrium(39) falls properly between Tb(65) and Tm(69).

Some of the data of Fig. 2 are presented in a different fashion in Figs. 3 and 4 in order to accent the Z effect.

In Fig. 3, the variation of log K, at a constant concentration of HNO_3 acid, with Z is shown for several different HNO_3 concentrations. The 18·5 M HNO_3 plot

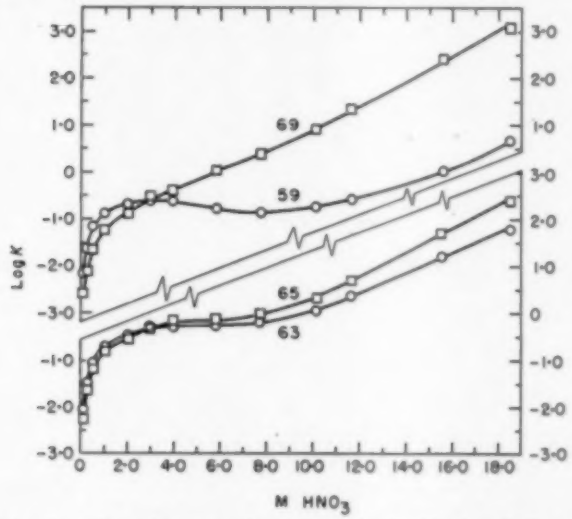

FIG. 1.—Extraction of certain symmetrically-placed lanthanides into TBP as a function of molarity of aqueous nitric acid.

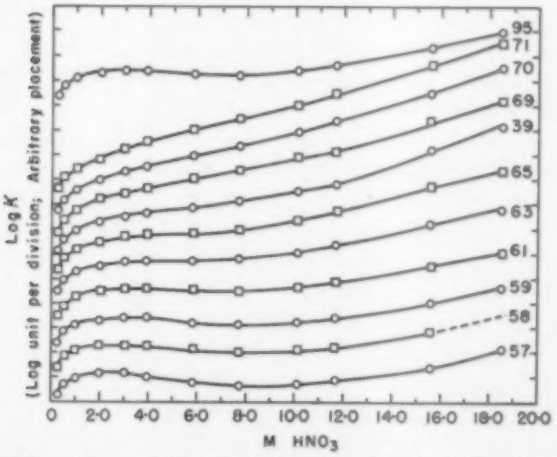

FIG. 2.—Extraction of lanthanides into TBP as a function of molarity of aqueous nitric acid. (Arbitrary placement for clarity and for comparisons.)

approximates a straight line. However, it is represented better by two straight lines meeting in the neighbourhood of $Z = 64$. (This curve does not contain a point for Ce, since it was found impossible to prevent partial oxidation of tracer-level Ce(III) to Ce(IV) in this acid medium, even in the presence of hydrogen peroxide.) It is to be noted that as the concentration of HNO_3 decreases, the slope of the right-hand

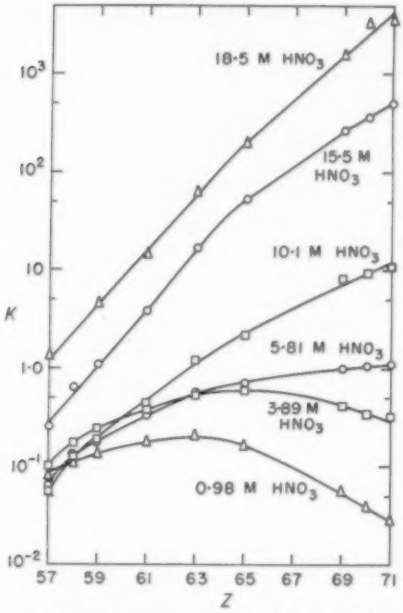

FIG. 3.—Extraction of lanthanides into TBP from aqueous nitric acid phases of selected molarity as a function of Z.

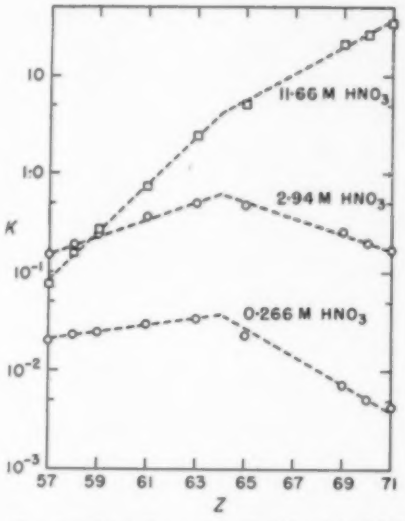

FIG. 4.—Extraction of lanthanides into TBP from aqueous nitric acid phases of selected molarity as a function of Z. (Arbitrary straight lines meeting at $Z = 64$.)

portion of the curve decreases more rapidly than does that of the left-hand portion until a definite inversion of some of the high-Z elements is demonstrated by the 3·89 M HNO_3 curve. This inversion is exaggerated at still lower HNO_3 concentrations, as shown by the 0·98 M HNO_3 curve.

This effect, ascribed to a behaviour as two subgroups, $Z = 57$–64 and $Z = 64$–71, is shown for other concentrations of HNO_3 in Fig. 4, in which two arbitrary straight lines, meeting at $Z = 64$, are drawn for each set of data. Whether these lines should be drawn with the point of intersection precisely at 64 is difficult to decide, and no trustworthy Gd tracer has been available for resolving the question. However, on the basis of the half-filled shell hypothesis,[5] it seems logical to draw the lines as in Fig. 4. Two points should be noted about Fig. 4. The curve, as drawn, for 2·94 M HNO_3 is essentially symmetrical about $Z = 64$; and the slope of the plot in the $Z = 57$–64 range never becomes negative, even at 0·266 M HNO_3.

From the fact (Figs. 1 and 2) that some of the lanthanides display a definite maximum followed by a definite minimum in the log K vs. M HNO_3 plot, it was considered likely that the dependence of K upon the TBP concentration was also a function of HNO_3 concentration. It was, therefore, decided to study the TBP dependence at two concentrations of HNO_3, one to the left of the maximum and one to the right of the minimum. The results are shown for 1·96 M HNO_3 in Figs. 5 and 7 and for 15·5 M HNO_3 in Figs. 6 and 8. The diluent used was carbon tetrachloride.

[5] H. BOMMER *Z. anorg. Chem.* **241**, 273 (1939).

From Figs. 5 and 6, it may be seen that the "half-filled shell effect" is operative in both concentrated TBP and dilute TBP systems involving these specific acid concentrations.

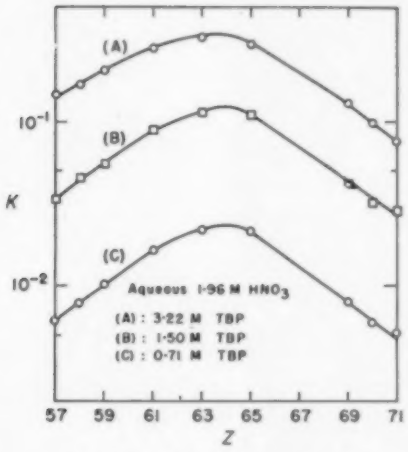

FIG. 5.—Extraction of lanthanides from aqueous 1·96 M HNO_3 into TBP phases of selected molarity. (Carbon tetrachloride diluent.)
Aqueous 1·96 M HNO_3
(A): 3·22 M TBP
(B): 1·50 M TBP
(C): 0·71 M TBP

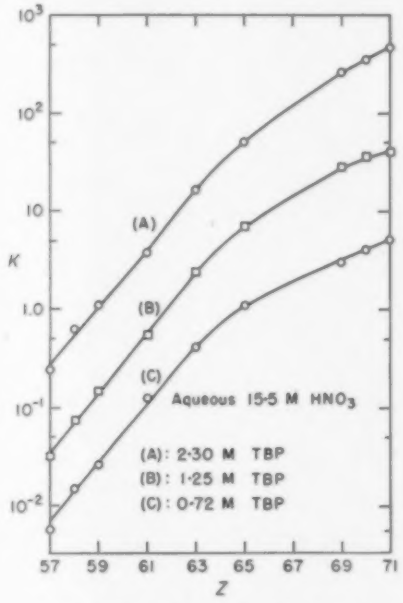

FIG. 6.—Extraction of lanthanides from aqueous 15·5 M HNO_3 into TBP phases of selected molarity. (Carbon tetrachloride diluent.)
Aqueous 15·5 M HNO_3
(A): 2·30 M TBP
(B): 1·25 M TBP
(C): 0·72 M TBP

From Fig. 7, it is seen that the dependence of K upon TBP concentration is approximately second power for the 1·96 M HNO_3 system, the arbitrary lines being drawn for second- and third-power dependencies. The high-Z and low-Z lanthanides appear to have essentially identical TBP dependencies at this acid concentration.

However, in Fig. 8, in which the arbitrary lines are drawn for second-, third-, and fourth-power TBP dependencies, it is seen that the K for a low-Z lanthanide approximates a third-power dependency while that for a high-Z lanthanide approximates a fourth-power dependency.

From the facts shown by Figs. 5–8, it seemed likely that a given pair of lanthanides for which Z was respectively less than 64 and greater than 64 should show inverted order of extraction at a considerably higher-acid concentration in a system involving diluted TBP than in one involving undiluted TBP. To test this hypothesis, an acid dependency study involving Eu(63) and Tm(69), using Am(95) as internal standard, was made using as solvent a solution made by diluting 25 volumes of pure TBP to 100 volumes with toluene and pre-equilibrating the resulting mixture with respect to the appropriate aqueous acid.

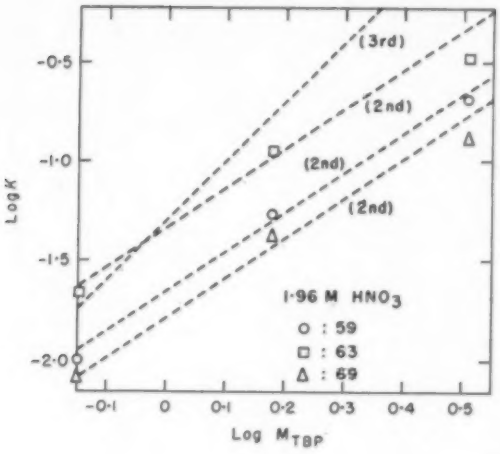

FIG. 7.—Extraction of selected lanthanides into TBP from aqueous 1·96 M HNO_3 as a function of molarity of TBP. (Carbon tetrachloride diluent.)
1·96 M HNO_3
○: 59
□: 63
Δ: 69.

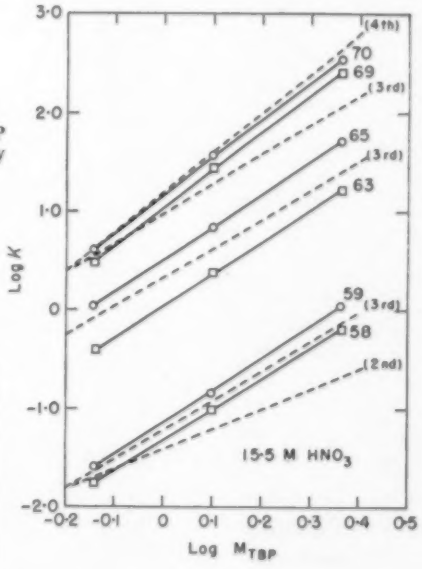

FIG. 8.—Extraction of selected lanthanides into TBP from aqueous 15·5 M HNO_3 as a function of molarity of TBP. (Carbon tetrachloride diluent.)
15·5 M HNO_3.

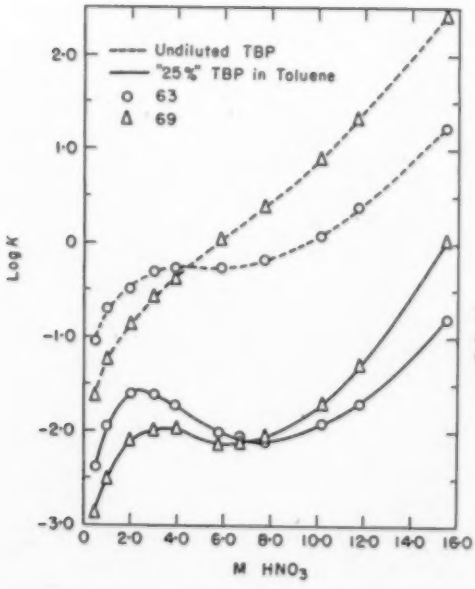

FIG. 9.—Comparison of extraction of elements 63 and 69 into: (A) "25%" TBP in toluene and (B) "100%" TBP, as a function of molarity of aqueous nitric acid.
— — — Undiluted TBP
——— "25%" TBP in Toluene
○: 63
Δ: 69.

The results, along with the 63 and 69 data from Fig. 1, are shown in Fig. 9. It may be seen that the 63 and 69 curves intersect at approximately 7·0 M HNO_3 as opposed to the intersection point at 4·5 M HNO_3 in the undiluted TBP system. It may be noted, further, that for the undiluted TBP system, each of the curves has a point of inflection in the 5–6 M HNO_3 region and that for the 25% TBP system each has both a maximum and minimum with a point of inflection at approximately 5 M HNO_3.

DISCUSSION

It is interesting to note that the various plots of log K vs. Z may be considered to approximate a composite of two straight-line portions meeting at $Z = 64$ and that, with decreasing HNO_3 concentration, the slope of the high-Z portion decreases more rapidly than does that of the low-Z portion. It is to be noted, further, that whereas, with decreasing HNO_3 concentration, the slope of the high-Z portion ultimately becomes negative, that of the low-Z portion remains positive throughout the region investigated.

When placed on these plots, Y falls at an apparent Z of 66–68, except for the plots in which the high-Z slope is nearly zero, in which case Y can not be placed with greater accuracy than 65–68. It follows, then, that on some plots in which the high-Z portion has a negative slope, Y will be double-valued with respect to apparent Z. For example, in the 2·94 M HNO_3 x undiluted TBP system the apparent Z values for Y are 60·6 and 67·6. However, it should be noted that the apparent Z for Y never assumes a value to the left of 64 unless it is double-valued.

It will be noted that even at 18·5 M HNO_3 the two portions of the plot do not form a continuous straight line. At 15·5 M HNO_3 the departure from a single straight line is quite marked. On the latter plot the apparent Z for Y is 67·6. However, if the Y value is plotted at 66·5 and only lanthanides of Z less than 65 are used in the plot, a single straight line results.

This half-filled shell effect has been shown by BOMMER[5] for a plot of ionic radius of lanthanide vs. Z and has been demonstrated by THOMPSON, CUNNINGHAM, and SEABORG[6] for the elution of both lanthanides and actinides from a Dowex-50 ion-exchange bed using a buffered citrate solution as elutriant. WHEELWRIGHT, SPEDDING, and SCHWARZENBACH[7] report a half-filled shell effect in their study of the stability of lanthanide complexes with ethylenediaminetetraacetic acid.

It is postulated that the extracting species is $[M(TBP)_a(H_2O)_{x-a}](NO_3)_3$ in which x is probably 6, but is conceivably dependent upon Z and smaller in the high-Z than in the low-Z range. The data are consistent with the assumption that the value of a approaches, in the neighbourhood of 2 M HNO_3, 2 for all Z values and, in the neighbourhood of 16 M HNO_3, 3 for low-Z nuclides and 4 for high-Z nuclides. Although the exact numbers are in some doubt, it is obvious that a considerable difference in TBP dependencies for Eu and Tm must be assumed in any explanation of the data of Fig. 9.

[6] S. G. THOMPSON, B. B. CUNNINGHAM, and G. T. SEABORG *J. Amer. chem. Soc.* **72**, 2798 (1950).
[7] E. J. WHEELWRIGHT, F. H. SPEDDING, and G. SCHWARZENBACH *Ibid.* **75**, 4196 (1953).

J. Inorg. Nucl. Chem., 1957, Vol. 4, pp. 334 to 343. Pergamon Press Ltd., London

FRACTIONAL EXTRACTION OF THE LANTHANIDES AS THEIR DI-ALKYL ORTHOPHOSPHATES*

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Abstract—The extraction of lanthanides(III) and yttrium(III) into a solution of di(2-ethyl hexyl) orthophosphoric acid (symbolized as HDEHP) in a carrier solvent from aqueous mineral acid phases has been investigated as a function of HDEHP concentration in the organic phase, mineral acid concentration in the aqueous phase, and Z, using the radioactive-tracer technique and employing americium as a normalizing element.

The distribution ratio, K, defined for a given radioactive nuclide as its concentration in the organic phase divided by its concentration in the aqueous phase, has been found to have a direct third-power dependency upon the HDEHP concentration in the organic phase and an inverse third-power dependency upon the mineral acid concentration in the aqueous phase. In experiments involving gross concentrations of extracting cation, it has been shown that none of the anion associated with this cation in the initial aqueous phase reports in the equilibrated organic phase. On the basis of these data, the extracting species has been formulated as $M(DEHP)_3$, possibly with solvate water.

Operationally, HDEHP may be considered as the high-acid analogue of thenoyl trifluoroacetone (symbolized as HTTA); and analogously the $M(DEHP)_3$ is tentatively considered to be a chelate complex.

A plot of log K vs. Z is well represented by a straight line of positive slope corresponding to an average value of r, defined as the ratio of K_{Z+1} to K_Z, of 2·5. This average r of 2·5, to be compared with the value of 1·63 as the ratio of molar aqueous solubilities of the dimethyl phosphates of adjacent lanthanides as reported by MARSH, is sufficiently large to make fractionation of lanthanides by liquid-liquid partition an attractive possibility. Successful application of such a technique to a gross sample has been demonstrated.

In the plot of log K vs. Z, Y falls on the straight line if given an artificial Z approximately 67·6, as it does in MARSH's plot of log molar solubility vs. Z for the lanthanide dimethyl phosphates.

IN THE course of the investigation of tri-*n*-butyl orthophosphate, $(n\text{-}C_4H_9O)_3PO$, symbolized as TBP, as an extractant for various tetravalent and trivalent lanthanides and actinides and for zirconium,[1a–c] present intrace concentrations, it was established that reproducible results were obtainable for the tetravalent species only if the solvent had been scrubbed with a basic aqueous phase (e.g. Na_2CO_3, NaOH, etc.) and if data were obtained shortly after pre-equilibration of the solvent with the pertinent aqueous mineral acid (e.g. HNO_3 or HCl). However, these precautions were not found necessary in the trivalent studies.

Following the proof[1d] that the effect on the tetravalent species was due to dibutyl phosphoric acid or to this ester and monobutyl phosphoric acid, both usually present in small concentrations in commercially available TBP and formed from TBP by acid-catalysed hydrolysis,[1d] samples of $(n\text{-}C_4H_9O)_2PO(OH)$, symbolized as HDBP,

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

(1) (a) D. F. PEPPARD, J. P. FARIS, P. R. GRAY, and G. W. MASON *J. phys. Chem.* **57**, 294 (1953); (b) D. F. PEPPARD, P. R. GRAY, and M. M. MARKUS *J. Amer. chem. Soc.* **75**, 6063 (1953); (c) D. F. PEPPARD, G. W. MASON, and J. L. MAIER *J. inorg. nucl. Chem.* **3**, 215 (1956); (d) D. F. PEPPARD and M. V. GERGEL *Argonne National Laboratory Report ANL*-4490 pp. 64-74 (1950).

and $(n\text{-}C_4H_9O)PO(OH)_2$, symbolized as H_2MBP, were obtained respectively from Commercial Solvents Corporation and Victor Chemical Works. Solvents prepared by dissolution of either of these agents in a carrier solvent such as benzene were found highly effective in the separation of thorium from the trivalent lanthanides by extraction from an acidic aqueous phase, the thorium reporting preferentially in the organic phase.

However, in establishing the conditions for routine thorium-lanthanide separations, using the dibutyl ester, it was discovered that a promising fractionation of the lanthanides was possible by use of the same chemical system.[2]

Further investigation showed di(2-ethyl hexyl)orthophosphoric acid, $[(C_2H_5)\text{-}C_6H_{12}O]_2PO(OH)$, symbolized as HDEHP, to be preferable to HDBP on the basis of greater resistance to hydrolysis and lower aqueous solubility.[2a] Consequently, the study presently reported was restricted principally to the use of HDEHP.

EXPERIMENTAL

Sources of materials

A mixture of the mono- and di-octyl orthophosphoric acids (2-ethyl hexyl isomers), consisting primarily of these acids, was obtained from Victor Chemical Works. This mixture was found to be essentially free from tri-octyl orthophosphate and octyl alcohol. It did, however, contain small quantities of pyro esters. The HDEHP and H_2MEHP were separated as described under "Purification of Solvents." The beta-active nuclides 40·2 h La^{140} (with parent 12·8 d Ba^{140}), 285 d Ce^{144}, 13·8d Pr^{143}, 11·6 d Nd^{147}, 2·6 y Pm^{147}, 47 h Sm^{153}, (13, 16) y $Eu^{152,154}$, 58 d Y^{91}, and 85 d Sc^{46} were obtained from the Isotopes Division of the Oak Ridge National Laboratory. The beta-active nuclides, 72 d Tb^{160}, 82 h Dy^{165}, 9·4 d Er^{169}, 129 d Tm^{170}, (32, 4·2) d $Yb^{169,175}$, and 6·8 d Lu^{177} were obtained from D. C. STEWART, of A.N.L., who prepared them by neutron irradiation of highly-purified lanthanides. All of the foregoing tracers were purified further by means of liquid-liquid extraction techniques. Alpha-active 470 y Am^{241} was obtained from A.N.L. stocks.

Purification of solvents

The HDEHP was separated, by a modification of the liquid-liquid extraction technique reported by STEWART and CRANDALL,[2] from the mixture consisting of the di-octyl and mono-octyl esters in approximately 60 : 40 mole ratio. Since, in the early stages of the investigation, it was discovered that traces of pyro esters greatly augmented the extractive power of either HDEHP or H_2MEHP, the mixture was stirred with a one-fourth volume portion of 6 M HCl at approximately 60°C for 16 hours to destroy pyro esters by hydrolysis. Following several water scrubs to remove HCl, the mixture was partitioned as follows, using diethyl ether and ethylene glycol as the opposing phases in a countercurrent extraction with scrubbing.[1c]

A physical system consisting of seven 2 l. separatory funnels, equipped with motor-driven stirrers, and mounted on a common support, and nine 1 l. beakers, supported on a common base which was linearly movable so that the nth beaker could be placed below the $(n-1)$th, the nth or the $(n+1)$th beaker, was used. Considering the contactors (funnels) to be numbered 1–7 consecutively from left to right, the ethylene glycol, feed (mixture of HDEHP and H_2MEHP), and diethyl ether were introduced into contactors 1, 4, and 7 respectively, using respective volumes of 750 ml, 100 ml, and 500 ml. A total of two litres of feed was cycled through the system.

The ether extracts were combined, washed with water to remove traces of ethylene glycol, and shaken with activated charcoal to remove unidentified coloured impurities. Following removal of the charcoal by filtration through a sintered-glass filter, the ether phase was subjected to room-temperature evaporation under reduced pressure leaving the HDEHP product.

[2] (a) JOHN L. MAIER Master's thesis (work directed by D. F. PEPPARD of A.N.L. and H. L. COLES of Michigan College of Mining and Technology) issued as *Argonne National Laboratory Report ANL*-WMM-1041 (1952); (b) D. F. PEPPARD, G. W. MASON, P. R. GRAY, J. L. MAIER, and M. M. MARKUS *Argonne National Laboratory Report ANL*-4873 p. 31. (1952); (c) D. F. PEPPARD, G. W. MASON, and J. L. MAIER *Argonne National Laboratory Report ANL*-4942 pp. 53-60 (1952).

[2] D. C. STEWART and H. W. CRANDALL *J. Amer. chem. Soc.* 73, 1377 (1951).

The combined ethylene glycol extract was diluted with an equal volume of water and the resulting solution contacted with three one-half volume portions of diethyl ether. The resultant combined diethyl ether extract was scrubbed with water to remove ethylene glycol, clarified with active charcoal, and evaporated as above to yield the H_2MEHP product.

Each of the products was identified by its titration characteristics, through use of a potentiometric technique with standard aqueous NaOH.[3] A 5-ml sample of the HDEHP product was added to a mixture of 25 ml of diethyl ether and 25 ml of ethylene glycol. Following an agitation period of 5 min, aliquots of each of the separated phases were titrated. The distribution ratio, K, for HDEHP into diethyl ether from ethylene glycol (concentration in upper phase divided by concentration in lower phase) was 15·0. In like manner, the corresponding K for H_2MEHP was determined as 0·20.

The products described above were demonstrated to be pure with respect to mutual contamination as shown by titration, with a probable limit of 3 mole per cent detection, and a calculation based on the K values indicated the probable H_2MEHP contamination of the HDEHP product to be well below 1 mole per cent. However, it was found that in studies involving this specific HDEHP product, the data for trace-level lanthanides differed markedly from those for gross-level lanthanides in the lower-Z range, whereas the two sets of data were in substantial agreement for the upper-Z range.

Consequently, the HDEHP product was considered as a new feed and processed twice more in a manner equivalent to the technique used in the initial separation. The H_2MEHP product was also subjected to two further purification cycles. In each case the product solvent, following the final purification, was found to exhibit identical behaviour in trace-level and gross-level lanthanide studies over the entire Z range. Unless otherwise noted, these final thrice-purified solvents were used in obtaining the data reported.

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Determination of distribution ratios

The distribution ratio, K, of a specific nuclide, defined as the concentration of nuclide in the upper divided by the concentration of nuclide in the lower of two equilibrated sensibly-immiscible liquid phases, was, in general, determined radiometrically. In the determination, a portion of aqueous acid of the indicated concentration containing one or more radioactive nuclides was equilibrated against a portion of solvent which had previously been pre-equilibrated with respect to the corresponding barren aqueous acid. For example, a 1 ml portion of 0·5 M HCl containing approximately 10^6 c/m of Pm^{147} and approximately 10^6 c/m of Am^{241} was contacted with a 1ml portion of 25% HDEHP-toluene (25 vol of HDEHP diluted to 100 vol with toluene). Aliquots of each phase were evaporated on 3-mil platinum discs 15/16 in. in diameter, by means of induction heating, for beta and alpha counting.

In instances in which Am^{241} was used as an internal normalizing nuclide the beta activity was counted through 10 mg of aluminium absorber. (A correction of 13 c/m per 10^3 c/m of Am^{241} was still required.) In instances in which Pm^{147} was used as an internal normalizing nuclide a great preponderance of Pm^{147} tracer was used so that only a small subtraction from the total measured activity was required in order to obtain that due to Pm^{147}. The activity of the accompanying nuclide was obtained by using 40 mg of aluminium absorber to lower the Pm^{147} contribution to a sufficiently low value to permit valid corrections.

Although, in experiments with Pm^{147}, it was demonstrated that equilibrium was attained in mixing periods of less than 30 sec, all data were obtained using 3 min mixing periods. The phases, in glass-stoppered 5 ml glass cylinders, were mixed by violent shaking, the two phases co-transferred to a centrifuge cone, the mixture centrifuged at full speed for a 1 min period in an International Clinical Centrifuge, Model CL, the lower phase transferred (by pipette) to a new centrifuge cone (leaving a small heel of lower phase to minimize the possibility of inclusion of traces of the upper phase), both phases centrifuged in their separate cones for a 1 min period, and aliquots of each phase then taken for analysis.

In several instances, the resulting pregnant organic extract was then contacted with fresh barren aqueous acid and a redetermination of K made to establish the fact that equilibrium had been attained.

All data were normalized to the average value obtained for the "normalizing element." If the data for the "normalizing element" differed internally by more than 10% from the average value, the experiment was repeated.

All data were obtained at 22 ± 2°C. Within this range, the variations in K were shown to be within experimental error.

Exploratory fractionations

The double-diamond method of operation referred to as pseudo countercurrent extraction by HUNTER and NASH[4] and as discontinuous countercurrent extraction by PEPPARD *et al.*,[1e] was employed as described by PEPPARD *et al.*,[1e] using a seven-stage assembly as described in the foregoing section entitled "Purification of Solvents." Contact and settling periods of 3 and 2 min respectively were used.

Extractions were continued for at least twice the number of cycles calculated, in approximate fashion, to be necessary for attainment of 90% of steady-state operation, basing the calculation on the K of the nuclide approaching steady-state most slowly, using the mathematical treatment of PEPPARD and PEPPARD.[5]

For assay of gross products, the metal content of the organic product phase was returned to an aqueous phase by re-extraction into 5 M HCl, following dilution of the solvent with an equal volume of benzene. These re-extracts and the pertinent aqueous product phases, following scrubbing with benzene to remove traces of HDEHP, were analysed by conventional procedures, the spectroscopic examinations being made by the copper-spark technique of FRED, NACHTRIEB, and TOMKINS.[6] In some instances, in order to increase the sensitivity of assay, a product was subjected to further extraction-separation before determination of contaminant.

RESULTS AND CONCLUSIONS

In establishing the behaviour of gross lanthanides, a 100-ml portion of 0·05 M aqueous $GdCl_3$ was equilibrated with a 100 ml portion of 0·75 M HDEHP in toluene. The separated organic phase was scrubbed with four successive 50-ml portions of water. The first depleted aqueous phase contained 5–8% of the total Gd, the first aqueous scrub contained less than 0·5% of the total Gd and showed a positive test for chloride ion, and the remaining aqueous scrubs gave no test for Gd, by NH_4OH precipitation or by oxalic acid precipitation, and gave no test for chloride ion. The organic extract was contacted with two successive 100 ml portions of aqueous 6 M HNO_3. The first of these aqueous re-extracts was found to contain 95–98% of the total extracted Gd, the second re-extract producing only a faint turbidity with NH_4OH. Neither re-extract gave a test for chloride ion.

The experiment was repeated twice more, utilizing, separately, $Gd(NO_3)_3$ and $Gd_2(SO_4)_3$ and using 3 M H_2SO_4 and 6 M HCl, respectively, as re-extractants. The results were essentially the same as those reported for the $GdCl_3$ experiment, the aqueous re-extracts failing to show a test for the anion initially associated with the feed material.

All three experiments were repeated exactly, using the corresponding Pr salts, except that 100 ml of 1·5 M HDEHP in toluene was used as the solvent and 500 ml of 0·01 M praseodymium salt as the feed. The results were essentially the same as those obtained in the Gd experiments.

From these data, it was established that the extracting lanthanide species contained the DEHP anionic entity and did not contain the anionic entity associated with the lanthanide in the original salt. As a working hypothesis, it was assumed that the formula of the extracting species is the simple M $(DEHP)_3$ or a more complex solvated variant. Tracer-level data are consistent with the simple formulation; however, data for gross lanthanides extracted under conditions permitting only a

[4] T. G. HUNTER and A. W. NASH *Industr. engng. Chem.* **27**, 836 (1935).
[5] D. F. PEPPARD and M. A. PEPPARD *Ibid.* **46**, 34 (1954).
[6] M. FRED, N. H. NACHTRIEB, and F. S. TOMKINS *J. opt. Soc. Amer.* **37**, 279 (1947).

low concentration of free HDEHP appear to be in conflict and indicate the solvated variant. This phase of the study is being extended.

In the plot of the tracer-level data, log K vs. Z, of Fig. 1, illustrating the extraction from 0·5 M HCl into 0·75 M HDEHP-toluene, the straight line indicates an average r of 2·5. (The symbol β is widely used to represent the ratio of the K values of two different nuclides and is so used in this paper. The symbol r is here used to represent specifically the ratio of the K values of adjacent lanthanides, the K

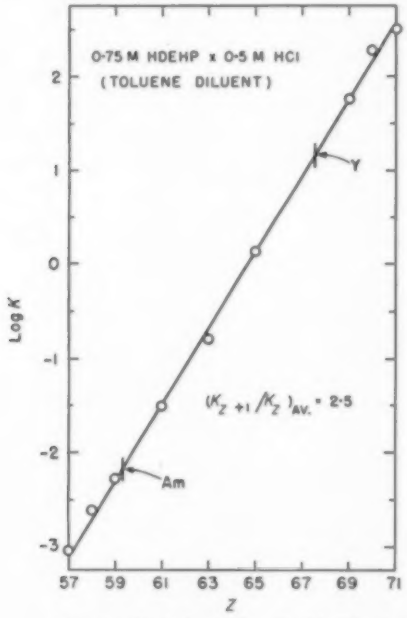

FIG. 1.—Variation of log K with Z in the 0·75 M HDEHP x 0·5 M HCl system. Placement of Y and Am included. (Toluene diluent.)

of element $Z = a + 1$ being divided by the K of element $Z = a$.) The β for the Lu-La pair is seen to be $3{\cdot}5 \times 10^5$.

This β-value of $3{\cdot}5 \times 10^5$ for the Lu-La pair may be compared with the corresponding β-value of $2{\cdot}1 \times 10^3$ for the undiluted tri-*n*-butyl orthophosphate–15·6 M HNO_3 system reported by PEPPARD, DRISCOLL, SIRONEN, and MCCARTY,[7] for which these authors report an average r of 2·0 in the La-Eu region and an average r of 1·5 in the Gd-Lu region. It may be noted that PEPPARD *et al.*[1a] reported an average r of 1·9 based on La, Ce, Pm, and Eu data and on erroneous assignment of the artificial Z of 66·5 to *Y*.

In other studies involving HNO_3 and H_2SO_4 respectively, it was established that the extraction of a given lanthanide is independent of the nature of the mineral acid, in the region tested. Therefore, the major portion of the data were obtained for systems involving HCl, since for gross studies the analyses were thereby simplified.

[7] D. F. PEPPARD, W. J. DRISCOLL, R. SIRONEN, and S. MCCARTY *J. inorg. nucl. Chem.* **4**, 326 (1957).

From Figs. 2 and 3 it may be seen that, under the conditions studied, the K for a given trivalent lanthanide has a direct third-power dependence upon the concentration of HDEHP in the equilibrated organic phase and an inverse third-power dependence upon the hydrogen-ion concentration in the equilibrated aqueous phase.

It may be noted from Fig. 1 that Y is somewhat to the left of Er when placed on the arbitrary straight line. It may be noted, further, from Figs. 2 and 3, that the HDEHP and aqueous acid dependencies of the K for Y are the same as those for the K for a true trivalent lanthanide.

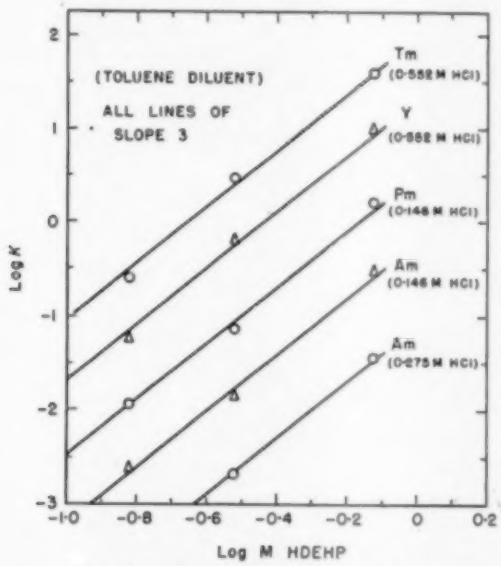

FIG. 2.—Variation of log K with log M HDEHP for Tm, Y, Pm, and Am at selected molarities of HCl. (Toluene diluent.)

The effect of traces of H_2MEHP is illustrated by the data of Fig. 4. The effect is negligible in the high-Z range, but noticeable at $Z = 63$, and very large in the region of $Z = 57$. The data for this curve were obtained using the "once-purified" HDEHP product as described under "Purification of Solvents."

A comparable curve was obtained by using a "thrice-purified" HDEHP product to which 1%, by weight, of "thrice-purified" H_2MEHP had been added before dilution with toluene. However, on the assumption that the effect shown in Fig. 4 is due solely to H_2MEHP, then the "once-purified" HDEHP must have contained somewhat less than 1% H_2MEHP contaminant.

On the basis of the data of Fig. 1, an exploratory fractionation of gross lanthanides was made as follows. A feed prepared by dissolving 83·3 g of Lindsay "75% Y_2O_3" in a slight excess of HCl and diluting to a volume of 1 l. to yield a solution approximately 0·3 M in free HCl was processed in a seven-stage system, as shown in Table 1. The "partitioning point," i.e. the Z below which less than 50% reports in the organic phase and above which more than 50% reports in the organic phase,[11a] is seen to be between Ho and Er, as calculated before the experiment was performed.

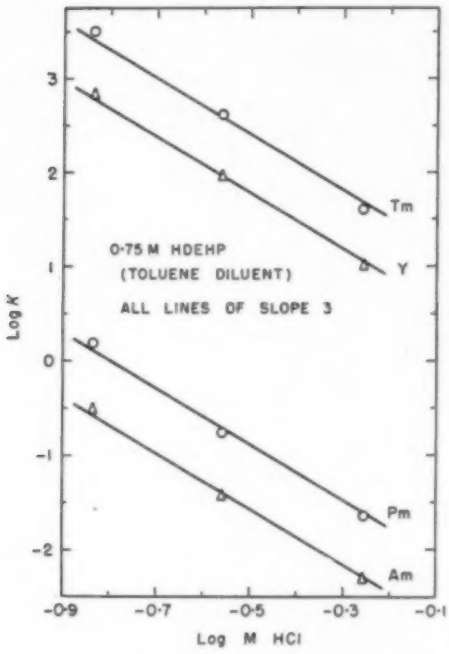

FIG. 3.—Variation of log K with log M HCl for Tm, Y, Pm, and Am in the 0·75 M HDEHP x HCl system. (Toluene diluent.)

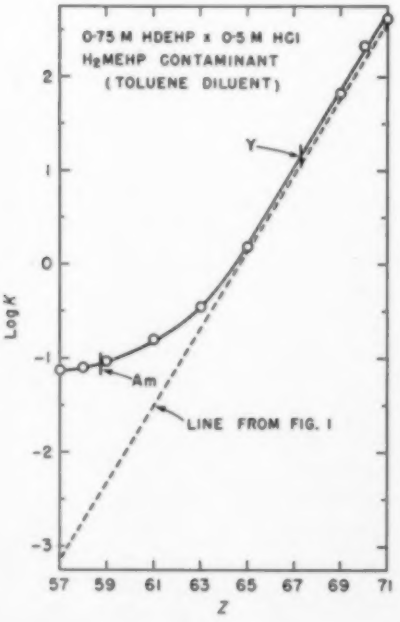

FIG. 4.—Variation of log K with Z in the 0·75 M HDEHP x 0·5 M HCl system, showing effect of H_2MEHP contaminant. Placement of Y and Am included. ("Once-purified" HDEHP in toluene diluent.)

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It is seen that the solvent phase contains Er (in greater than 90% yield) decontaminated from Dy by a factor of approximately 13. The corresponding decontamination factor with respect to Gd is greater than 35.

The HCl and HDEHP-toluene system has also been used in the mutual separation of certain fission-product lanthanides. For example, the 1·5 M HDEHP and 0·25 M HCl system, the 1·5 M HDEHP and 0·50 M HCl system, and the 0·75 M HDEHP and 0·50 M HCl system were used respectively for separating the Ce-Pm pair, the

TABLE 1.—PARTITION OF A LINDSAY "75% Y_2O_3" SAMPLE INTO TWO FRACTIONS
20 ml FEED (0·3 M HCl), 20 ml SCRUB (1·0 M HCl), 40 ml SOLVENT
(50% HDEHP in toluene). $q = 7$, $n = 4$. Solvent yield of Y: ~90%

	Composition (relative mass normalized to yttrium = 1000)												
	Y	La	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Feed	1000	5	5	8	1	200	60	500	70	120	20	50	3
Solvent product	1000	<1	<5	<5	<1	<5	<5	35	20	110	20	50	2
Aqueous product	1000	50	60	100	20	2500	600	3000	300	30	<10	<2	<1

Pm-Eu pair, and the Eu-Y pair. These three systems have been used in the purification of certain tracers used in this study. The 1·5 M HDEHP and 0·10 M HCl system has also been used to separate Am^{241} from gross La, which had been employed in the initial isolation of Am^{241}.

The data for Am^{241} have been included in order to establish the validity of using this nuclide as a normalizing element.

DISCUSSION

The extraction of the lanthanides into HDEHP + diluent from an aqueous phase may be expressed, to a close approximation, by the following equations:

$$M_A^{+3} + 3HDEHP_O \rightleftharpoons M(DEHP)_{3_O} + 3H_A^+ \quad (1)$$

$$[M(DEHP)_3]_O/[M^{+3}]_A = k_E[HDEHP]_O^3/[H^+]_A^3 \quad (2)$$

$$K = [M(DEHP)_3]_O/[M^{+3}]_A \text{, assumed} \quad (3)$$

$$K = k_E[HDEHP]_O^3/[H^+]_A^3 \quad (4)$$

where the subscripts A and O refer, respectively, to equilibrated aqueous and organic phases, and the bracketed quantities refer to concentrations expressed in molarity units, in the absence of pertinent activity data.

The postulated chelate formation is shown in Table 2 and compared with the postulated chelate formation involving TTA, thenoyl trifluoroacetone.[8] (No attempt to differentiate the various resonance structures has been made.)

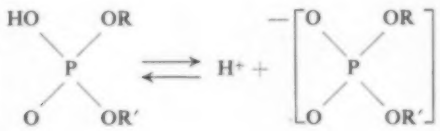
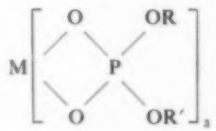
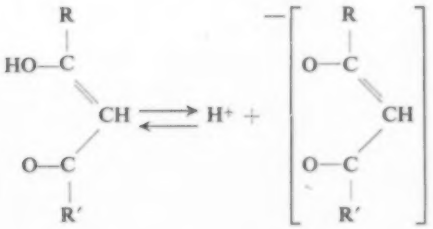
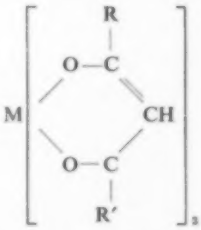
The tracer data show solvent and aqueous acid dependencies consistent with equation (4), and the gross data show the extracted species to contain no anionic entity other than DEHP.

[8] (a) J. C. REID and M. CALVIN *Atomic Energy Commission Document* MDDC-1405; (b) F. HAGEMANN *J. Amer. chem. Soc.* **72**, 768 (1950).

Although the formulation as a chelate in Table 2 cannot be considered as established, the very large values of k_E seem indicative of chelation, and the objection that a four-membered ring is involved is met with the established existence of four-membered rings in the various Co(III) complexes containing the $CO_3^=$ group. Consequently, the complex has been formulated, tentatively, as a chelate.

The study is being extended; and the data of exploratory gross experiments indicate solvent saturation, in the low hydrogen-ion concentration range, at a 1 : 6 mole ratio of M^{+3} to HDEHP, the attempted introduction of additional M^{+3} into the organic phase resulting in the formation of an amorphous solid. These data

TABLE 2.—COMPARISON OF DIALKYL ORTHOPHOSPHORIC ACID AND BETA DIKETONE EXTRACTION MECHANISMS

Specific reagent	General dissociation	M(III) complex (postulated)
HDEHP		
HTTA		

are consistent with the assumption of $M(DEHP)_3(HDEHP)_3$ or $M[H(DEHP)_2]_3$ as the extracting species, the latter corresponding to chelation by mono-ionized dimeric di(2-ethyl hexyl)orthophosphoric acid.

It is of interest to note that MAGNUSSON and ANDERSON[9] report the extraction of Yb(III) and Eu(III) from a monochloroacetate-buffered aqueous phase into a TTA-in-toluene phase, the ratio of the respective *K*-values for Yb(III) and Eu(III) being approximately 7. The corresponding ratio in Fig. 1, for a HDEHP—HCl system, is seen to be approximately 1000.

It is of interest also to compare the solvent-extraction-fractionation of the lanthanides as the di-octyl phosphates with their fractionation by crystallization as the dimethyl phosphates as initially reported by MORGAN and JAMES[10] and more completely by MARSH.[11] MARSH[11b] finds the aqueous solubility of the Gd-Lu sequence

[9] L. B. MAGNUSSON and M. L. ANDERSON *J. Amer. chem. Soc.* **76,** 6207 (1954).
[10] J. C. MORGAN and C. JAMES *Ibid.* **36,** 10 (1914).
[11] (a) J. K. MARSH *J. chem. Soc.* **1934,** 1972; (b) *Ibid.* **1939,** 554.

to decrease with increasing Z, so that a plot of log solubility (on a mole basis) vs. Z yields a straight line of negative slope approximating $-1{\cdot}63$ at 25°C. The value for Y falls on this line, if Y is given the artificial atomic number 67·6.

It may be seen, from Fig. 1, that in the HDEHP x HCl system, Y also falls on the line if given an artificial atomic number approximately 67·6.

It is felt that the HDEHP (in diluent) x mineral acid system offers considerable promise in lanthanide separations technology due to the steepness of the log K vs. Z curve (average $r = 2{\cdot}5$, Fig. 1), which serves to lower the number of stages required in countercurrent operation to a reasonable number. This r of 2·5 may be compared with the value of 1·63 as the ratio of molar solubilities of the dimethyl phosphates of adjacent lanthanides[11] and with the maximum r of 1·9 in the TBP-HNO_3 extraction system.[7]

The data of Table 1 demonstrate the feasibility of the general lanthanide separation. It is evident that any desired degree of mutual separation of a given pair of lanthanides may be achieved by use of the proper number of stages and that any lanthanide may be separated from all other lanthanides by a double processing, in which the respective conditions are such that the desired lanthanide reports in the one phase (either aqueous or organic) in the first separation and in the opposing phase in the second. It is, further, evident that the separation of pure Ho or Er is made difficult by the Y interference. Conversely, this system offers an attractive means for separation of yttrium from all lanthanides other than Ho and Er.

From an analysis of the data of Fig. 1 and Table 1, it appears that satisfactory separation of the lanthanides should be accomplished by a thirty-stage countercurrent extraction using the HDEHP (diluent) x mineral acid systems. Equipment to test various flow sheets involving such systems is being fabricated.

Investigation of the application of H_2MEHP (diluent) x mineral acid systems to lanthanide fractionation is being extended. It has been established that for such systems the plot of log K vs. Z departs from a straight line radically. The application of both HDEHP and H_2MEHP to the fractionation of actinides is being investigated.

In considering HDEHP for new applications, it is helpful to consider it as the "high-acid" analogue of HTTA. For example, the HTTA extractions reported by HAGEMANN[8b] for Th(IV), Ac(III), and Ra(II) may be duplicated by HDEHP systems involving a much more acidic aqueous phase. In those instances in which hydrolysis reactions may interfere with a separation, the use of HDEHP is, therefore, indicated.

J. Inorg. Nucl. Chem., 1957, Vol. 4, pp. 344 to 348. Pergamon Press Ltd., London

ISOLATION OF BERKELIUM BY SOLVENT EXTRACTION OF THE TETRAVALENT SPECIES*

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(*Received* 21 *January* 1957)

Abstract—Data for the extraction of Cm(III), Bk(III), and Bk(IV) into a *n*-heptane solution of di(2-ethyl hexyl) orthophosphoric acid from various aqueous nitric acid phases are presented. The *K* value for Bk(IV) is greater than that for Bk(III) or Cm(III) by a factor approaching 10^6. Under the oxidizing conditions used, Am remains in the trivalent state.

A flow sheet utilizing this solvent extraction system and involving both the trivalent and tetravalent states of Bk has been devised. Using a raw berkelium fraction, isolated in the preliminary processing of an exhaustively neutron-irradiated plutonium sample, as feed, a Bk^{249} product was isolated in approximately 97% yield with established alpha decontamination factor and beta decontamination factor of approximately 6×10^3 and 9×10^5 respectively. The total processing time, exclusive of evaporation, was less than 30 min.

In an experiment involving the same flow sheet and a synthetic feed, it was demonstrated that Bk may be separated rapidly and satisfactorily from all of the following: La, Pm, Eu, Y, U, Np, Pu, Am, and Cm. Elements of *Z* greater than 97 were not available for testing, but it appears certain that Bk would be satisfactorily separated from any of these present in the trivalent state.

It is suggested that this solvent-extraction procedure should be useful not only for the isolation of Bk from source materials, but also in milking experiments in which a Bk isotope is either the mother or daughter, especially in studies in which one or more of the nuclides involved is short-lived.

SINCE, in its trivalent state, berkelium exhibits the behaviour of a typical actinide, it seems logical to exploit the tetravalent state, reported by THOMPSON, CUNNINGHAM, and SEABORG,[1] in order to effect the required separation.

In the study here reported, a technique was developed based on the fact that under controlled conditions, tetravalent and hexavalent members of the lanthanide and actinide series may be extracted efficiently from an aqueous nitric acid phase into an opposing phase containing di(2-ethyl hexyl) orthophosphoric acid, whereas the trivalent members of these groups remain preferentially in the aqueous phase.

Americium and berkelium are unique among the elements of atomic number 95–100 in that they may exist in oxidation states higher than 3 in aqueous solution. Since, both in the elucidation of decay schemes and in the separations involved in the processing of bombarded targets, the need for a clean and rapid separation of element Z from any or all elements in the range of $Z - 2$ to $Z + 2$ frequently arises, these extra oxidation states have been used to great advantage by a number of workers. The present study involves the application of liquid-liquid partition to the processing of samples containing berkelium, the oxidation system being such that berkelium is oxidized to the tetravalent state, but americium remains in the trivalent state.

EXPERIMENTAL

General. Di(2-ethyl hexyl) ortho phosphoric acid, represented by $(C_8H_{17}O)_2PO(OH)$ and symbolized as HDEHP, was obtained from Victor Chemical Works in the form of a nearly-equal-molar

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

[1] S. G. THOMPSON, B. B. CUNNINGHAM, and G. T. SEABORG *J. Amer. chem. Soc.* **72**, 2798 (1950).

mixture of the di- and mono-esters. It was separated from the mixture and prepared for use by liquid-liquid partition between diethyl ether and ethylene glycol following the general procedure reported by STEWART and GRANDALL.[2] The diluent used was *n*-heptane obtained from Phillips Petroleum Company. The 290 d beta-active Bk^{249} source material was obtained from P. F. FIELDS of A.N.L. The alpha-active actinides $3{\cdot}4 \times 10^4$ y Pa^{231}, $1{\cdot}6 \times 10^5$ y U^{233}, $2{\cdot}2 \times 10^6$ y Np^{237}, $2{\cdot}4 \times 10^4$ y Pu^{239}, 470 y Am^{241} and 18 y Cm^{244} were obtained from A.N.L. stocks. The beta-active nuclides 40 h La^{140}, 2·6 y Pm^{147}, (13, 16) y $Eu^{152, 154}$ and 58 d Y^{91} were obtained from the Isotopes Division of the Oak Ridge National Laboratory. (The La^{140} was separated from its parent Ba^{140} before use.)

Determination of K. The determination of the distribution ratio, *K*, defined for a given nuclide as the ratio, on a radioactivity basis, of the concentration of nuclide in the upper to the concentration of nuclide in the lower of two sensibly-immiscible liquid phases was determined as in previous studies,[2] except as noted. Aliquots of each phase were evaporated on small platinum discs for radioactive assay.

Alpha-counting was done with an internal proportional counter. The background counting rate was 1·1 c/m. For determination of high-level hard-beta contamination, an end-window proportional counter with a 14·28 mg aluminium absorber was used. For determination of low-level hard-beta content, an end-window proportional counter with anti-coincidence with a 14·28 mg aluminium absorber was used. The respective background counting rates were 11 c/m and 2·3 c/m. For determination of the soft betas of Bk^{249}, an internal continuous-flow type of counter with anticoincidence was used. The background counting rate was 2·7 c/m. These three counters were mutually calibrated.

Over a fifty-fold range in concentration of nuclide, no variation in *K* was noted. All experiments were performed at $22 \pm 2°C$.

Oxidation and reduction. The oxidation of Bk was accomplished by use of $KBrO_3$ in 10 M HNO_3 or by use of a HDEHP-heptane solution which had been pre-equilibrated against a solution of $KBrO_3$ in 10 M HNO_3. Reduction was accomplished by means of H_2O_2 in HNO_3 or in HCl. Both oxidation and reduction were performed at room temperature. In all extraction experiments involving Bk(IV), the HDEHP-heptane solvent was pre-equilibrated against the pertinent aqueous phase, 10 M HNO_3 + 1 M $KBrO_3$ or 10 M HNO_3 + 0·1 M $KBrO_3$, by contacting with three equal-volume portions of the latter in order to remove reducing impurities and, in some instances, to produce an oxidizing solvent.

RESULTS

Various Bk^{249} source materials, resulting from the processing of exhaustively neutron-irradiated plutonium samples,[4] were obtained from P. F. FIELDS. One of these, "Berkelium Source Material-1," thought to contain of the order of 10^5 c/m of Bk^{249} and containing greater than 10^6 c/m of hard-beta activity and greater than 10^6 c/m of alpha activity, was processed as follows.

The sample was evaporated several times to near-dryness with 16 M HNO_3 and finally converted to a feed, *Feed*-1, which was 10 M in HNO_3 and 1 M in $KBrO_3$ and of 2-ml volume. The *oxidizing scrub* was a freshly-prepared aqueous phase 10 M in HNO_3 and 1 M in $KBrO_3$. The *reducing scrub* was a freshly-prepared aqueous phase 8 M in HNO_3 and 1·5 M in H_2O_2. The *solvent* was a 0·15 M HDEHP-heptane solution which had been freshly pre-equilibrated against three equal-volume portions of oxidizing scrub. All phases were used in 2 ml portions. All contacting periods were of 3 min duration. A portion of solvent was successively contacted with a portion of Feed-1 and two portions of oxidizing scrub. The three resulting aqueous phases were combined as *aqueous waste*-1. The pregnant solvent was contacted with a portion of reducing scrub, which in turn was contacted successively with a portion of fresh

[2] D. C. STEWART and H. W. CRANDALL *J. Amer. chem. Soc.* **73**, 1379 (1950).
[3] D. F. PEPPARD, J. P. FARIS, P. R. GRAY, and G. W. MASON *J. phys. Chem.* **57**, 294 (1953) and D. F. PEPPARD, P. R. GRAY, and M. M. MARKUS *J. Amer. chem. Soc.* **75**, 6063 (1953).
[4] L. B. MAGNUSSON, M. H. STUDIER, P. R. FIELDS, C. M. STEVENS, J. F. MECH, A. M. FRIEDMAN, H. DIAMOND, and J. R. HUIZENGA *Phys. Rev.* **96**, 1576 (1954).

solvent and a portion of heptane. The resulting aqueous phase was labelled *product*-1. The resulting organic phases were combined as *solvent waste*-1.

The data are given in Table 1. Product-1 was identified as essentially pure Bk^{249}, on the basis of its decay characteristics and ion-exchange behaviour, by RUTH SJOBLOM of A.N.L.

TABLE 1.—EXTRACTION OF Bk^{249} FROM "BERKELIUM SOURCE MATERIAL-1" FOLLOWING CONVERSION TO FEED-1

Phase	Activity in total phase (c/m)		
	Alpha	Hard beta	Soft beta
Aqueous waste-1	$1{\cdot}4 \times 10^6$	$1{\cdot}7 \times 10^5$	N.D.*
Organic waste-1	$2{\cdot}1 \times 10^5$	$4{\cdot}7 \times 10^3$	N.D.*
Product-1	$2{\cdot}7 \times 10^2$	$1{\cdot}8 \times 10^2$	$2{\cdot}8 \times 10^5$

* N.D. signifies not detected.

The solvent waste-1 was contacted with four portions of reducing scrub, the resulting aqueous phases added to aqueous waste-1, and the combined aqueous phases converted to *feed*-2, which was 10 M in HNO_3 and 1 M in $KBrO_3$. Feed-2 was then processed in a manner identical to that used for feed-1. The resulting *product*-2 contained 9×10^3 c/m of Bk^{249}. It seems likely, therefore, that the yield of Bk^{249} in product-1 approximated 97%.

The major portion of product-1 was then subjected to a second purification cycle identical to that used for feed-1. The yield was in excess of 99%. The total product contained $2{\cdot}4 \times 10^5$ c/m of Bk^{249}, less than 10 c/m of alpha activity, and less than 70 c/m of hard-beta activity. This final product Bk^{249} was used in determination of the *K* values of Table 2 and in the separation reported in Table 3.

TABLE 2.—EXTRACTION OF Cm(III), Bk(III), AND Bk(IV) INTO 0·15 M HDEHP-HEPTANE FROM AQUEOUS HNO_3

Aqueous phase	*K*		
	Cm(III)	Bk(III)	Bk(IV)
10 M HNO_3	$1{\cdot}5 \times 10^{-3}$	$2{\cdot}3 \times 10^{-3}$	—
10 M HNO_3, 0·1 M $KBrO_3$	$1{\cdot}5 \times 10^{-3}$	—	$1{\cdot}9 \times 10^3$
10 M HNO_3, 1 M $KBrO_3$	$1{\cdot}4 \times 10^{-3}$	—	$1{\cdot}8 \times 10^3$
10 M HNO_3, 1·5 M H_2O_2	$1{\cdot}4 \times 10^{-3}$	$2{\cdot}2 \times 10^{-3}$	—
8 M HNO_3, 1·5 M H_2O_2	$1{\cdot}7 \times 10^{-3}$	$2{\cdot}5 \times 10^{-3}$	—

From Table 2 it may be seen that the ratio of the Bk(IV) *K* to the Bk(III) *K* is approximately 10^6 and that the Cm(III) *K* differs only slightly from the Bk(III) *K*. It should be noted that determination of the Bk(IV) *K* in the absence of an oxidizing agent such as $KBrO_3$ proved impossible due to rapid reduction, presumably by trace reductants in the solvent. It should be noted further that the Bk(III) and Cm(III)

data may well be in error by perhaps 10–25%, since no effort has been made to obtain exact values.

However, it has been established that under the conditions given in Table 2, Bk(III) is more extractable than Cm(III). It has been established further that under these conditions all of the trivalent lanthanides and all of the trivalent actinides up to Bk (the highest number available to us for study) have K values much lower than that of Bk(IV) and that tetravalent Ce, tetravalent and hexavalent actinides, and pentavalent Pa have K values much greater than that of Bk(III).

On the basis of these data, a separation of a synthetic mixture was performed, using the flow sheet described for the isolation of product-1 of Table 1. The results are given in Table 3. Runs *C*, *B*, and *A* respectively involved a complete synthetic feed, the same synthetic feed without Bk, and pure Bk.

TABLE 3.—ISOLATION OF Bk^{249} FROM A SYNTHETIC MIXTURE BY USE OF A 0·15 M HDEHP-HEPTANE AND HNO_3 SYSTEM*

Valence	Decay type	Elements (Elements present at makeup of synthetic feed, SF (~$2{\cdot}5 \times 10^5$ c/m of each in indicated valence states))
III	Beta	La, Pm, Eu, Y, Bk ($2{\cdot}4 \times 10^5$ c/m)
III	Alpha	Am, Cm, Pu
IV	Alpha	Np, Pu
V	Alpha	Pa
VI	Alpha	U, Np, Pu

Run	Feed	Activity in total product (c/m)		
		Alpha	Hard beta	Soft beta
A	Only Bk ($2{\cdot}4 \times 10^5$ c/m)	$0{\cdot}6 \times 10^3$	$1{\cdot}2 \times 10^3$	$2{\cdot}4 \times 10^5$
B	Barren SF (without Bk)	$4{\cdot}8 \times 10^2$	$1{\cdot}7 \times 10^2$	—
C	SF	$3{\cdot}9 \times 10^2$	$2{\cdot}2 \times 10^2$	$2{\cdot}4 \times 10^5$

It may be noted that the trivalent contaminants report principally in the depleted aqueous feed and partially in the scrubs and that all others report principally in the first solvent and partially in the second solvent. (The purpose of the final heptane contact is to remove residual HDEHP from the product phase.)

For certain specific studies it is desirable to avoid the introduction of metallic ions. In these instances, a satisfactory extraction of Bk may be obtained by contacting a 10 M HNO_3 Bk feed (containing no $KBrO_3$) with an oxidizing solvent, prepared by equilibrating a 0·30 M HDEHP-heptane solvent with three equal-volume portions of oxidizing scrub. This pregnant solvent phase may then be scrubbed with 10 M HNO_3 scrubs which have been *freshly-contacted* with oxidizing solvent. A repeat of the

* Flow sheet identical to that described for isolation of Product-1 of Table 1.

experiment of Table 3 involving a flow-sheet modified in this manner yielded product of purity nearly equal to that of the product of Table 3, but in only 60% yield.

It was demonstrated that the 1 M $KBrO_3$ may be replaced by 0·1 M $KBrO_3$ in the flow-sheet described for Table 1. A product isolated from "Berkelium source material-2" by use of this modified flow-sheet was obtained in greater than 90% yield and was of purity comparable to that of product-1, Table 1.

It should be noted that Bk cannot be separated from Ce by use of any of the foregoing systems.

Attempts to use HIO_3 as the oxidant were unsuccessful, less than 5% extraction of the Bk being achieved using a 10 M HNO_3, 0·5 M HIO_3 aqueous phase and 0·15 M HDEHP-heptane as solvent and either 30-min contacting at 22°C or 10-min contacting at 60°C.

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SOLVENT DISTRIBUTION STUDIES OF THE CHEMISTRY OF ASTATINE

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Abstract—Certain aspects of the chemistry of the positive oxidation states of astatine have been investigated by solvent distribution studies. The existence of a chlorocomplex, probably $AtCl_2^-$, has been established. Methods for the recovery of astatine from inorganic residues, and for the isolation of astatine from bismuth targets, have been based on the ether extractability of this complex. Some organic reactions attributable to HAtO have been observed.

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PRESENT knowledge of the chemistry of the synthetic element astatine is very limited. The solvent distribution experiments reported here were undertaken as part of an investigation of the positive oxidation states of this element. The experiments were designed in anticipation of similarities between astatine and the other halogens, and the interpretation of the results are in terms of the expected analogy.

EXPERIMENTAL

The cyclotron of the Argonne National Laboratory was used to produce the astatine. Bombardment of bismuth metal with 43-MeV helium ions produced At^{211} by $(\alpha,2n)$ reaction, and At^{210} by $(\alpha,3n)$ reaction. The thick-target yields were 4·0 mc of At^{210} and 3·1 mc of At^{211} per microampere-hour of bombardment.

Two methods of isolation were employed. Heating the bismuth metal to its melting-point causes volatilization of the astatine from the molten target;[1,2] a stream of N_2 then carried the astatine through a series of traps. Various traps used were U-tubes in liquid nitrogen, U-tubes in dry ice-acetone, or aqueous solutions of NaOH. The second method of isolation will be described below.

The *iso*propyl ether used was reagent grade; it had been washed three times with a saturated $FeSO_4$ solution and then three times with water 1 or 2 days prior to use in the experiments reported. Reagent-grade carbon tetrachloride, phenol, and benzene were used without further purification, unless otherwise indicated below. Four different supplies of water were used at various times: singly distilled, doubly distilled, deionized by ion exchanger, and one deionized and then distilled. No results were obtained that suggested that any one of these sources was superior to the others; if spurious results have been caused by the presence of impurities, all sources must be contaminated alike.

The γ rays from At^{210} were used for detection purposes, since this method allowed direct counting of solutions. In the distribution experiments, equal volumes of the two solvents were mixed. The results of these experiments are stated in terms of the per cent of activity appearing in each phase; these values are not convertible to distribution coefficients in cases where volume changes occur on mixing. Large volume changes occur for the *iso*propyl ether-hydrochloric acid equilibrations reported. The concentration of astatine in the distribution experiments was generally in the region of 10^{-12} molar. The astatine isolated displayed the proper decay characteristics for At^{210} and At^{211}, and the data have been corrected for decay where comparisons over a period of time are involved.

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[1] G. L. JOHNSON, R. F. LEININGER, and E. SEGRÈ *J. chem. Phys.* **17**, 1 (1949).
[2] M. W. PARROTT, W. M. GARRISON, P. W. DURBIN, M. JOHNSTON, H. S. POWELL, and J. G. HAMILTON UCRL-3065.

EXPERIMENTAL RESULTS

Evidence for a chloro-complex. Two chloro-complexes of iodine, ICl_2^- and ICl_4^-, are known. It is also known that the former can be extracted into ethers from HCl solutions,[3] and the same behaviour would be expected for ICl_4^-. It would be reasonable that the ions $AtCl_2^-$ and $AtCl_4^-$, if they could be formed, should show the same behaviour. Although they should be extractable into ethers, they should not be extracted into benzene or carbon tetrachloride. These expectations have been realized when astatine is oxidized in fairly strong hydrochloric acid. The extractive behaviour of three separate preparations is shown in Table 1.

TABLE 1.—EXTRACTION OF A CHLORO-COMPLEX BY ORGANIC SOLVENTS
(per cent extracted)

Initial molarity. HCl	Solution A		Solution B		Solution C	
	*Iso*propyl ether	Benzene	*Iso*propyl ether	Benzene	*Iso*propyl ether	CCl_4
1	39	13	32	4	—	—
2	56	1·4	56	1·8	—	—
3	56	<0·2	—	<0·2	53	—
4	60	<0·2	—	—	—	—
5	70	<0·2	—	—	72	—
6	78	<0·2	75	—	75	<0·2
7	84	<0·2	—	—	—	—
8	87	<0·2	80	—	—	<0·2
9	85	<0·2	—	—	—	—
10	71	<0·2	68	—	—	—
11	31	<0·2	—	—	—	—
12	18	<0·2	—	—	—	<0·2

The solutions were prepared as follows:

Solution A. The astatine was originally present in neutral solution as a mixture of several simple inorganic forms. Hydrochloric acid was added to bring its concentration to 6 M, and gaseous Cl_2 was bubbled through the solution for 30 min. The solution was extracted five times with CCl_4 to remove Cl_2.

Solution B. The bismuth target was dissolved in HNO_3, the solution concentrated, and HCl added to bring its concentration to 9 M. The activity was extracted into *iso*propyl ether, the ether phase was washed with 8 M HCl, then back-extracted with 0·5 M NaOH. The basic solution was allowed to stand 6 hours at room temperature.

Solution C. Residues from several oxidation-reduction reactions were combined and concentrated. All of the astatine was in inorganic form. The solution was 2 M in HCl, and iron was absent. Gaseous Cl_2 was bubbled through the solution for 15 min. The solution was made 9 M in HCl and extracted with *iso*propyl ether. The ether phase was washed with 8 M HCl, then back-extracted with 1 M NaOH. The basic solution was placed in an 80° bath for 90 min.

Small aliquots of the solutions were then added to twenty times their volume of the appropriate HCl solution. Under these conditions "salting out" by substances other than HCl should be negligible.

[3] M. P. SCHUTZENBERGER *Compt. rend.* **84,** 389 (1877); A. E. GILLAM and R. A. MORTON *Proc. roy. Soc.* **A132,** 152 (1931).

The similarity in behaviour of these solutions suggests that a single complex of astatine is involved, and that for solutions greater than 3 M in HCl, essentially all of the astatine is in the form of the complex anion. The changes in extractability with acidity for the ether, and the appearance of the maximum extraction at 8–9 M HCl, are characteristic of the hydrochloric acid-*iso*propyl ether system when used for such extractions,[4] and hence do not require the postulation of additional astatine species for their explanation.

The presence of some HNO_3 has little effect on the ether extraction; when an 8 M HCl–0·8 M HNO_3 solution was used as the initial aqueous phase, 91% of the activity was extracted. The effect of fluoride ion on the extraction was tested by attempting back-extraction from an ether solution previously equilibrated with an 8 M HCl solution of astatine.

Washing solution	Per cent back-extracted
8 M HCl	23
7 M HCl	26
7 M HCl–0·5 M HF	27

Fluoride is seen to have little effect on the extraction in these concentration ranges.

Solutions of the complex in HCl, allowed to stand open to the atmosphere at room temperature, do not lose astatine by volatilization over a period of 3 hours. This, in addition to the extractive behaviour with benzene and CCl_4, suggests that only a small fraction of the astatine is present as neutral molecules such as AtCl or $AtCl_3$. When distilled, such solutions lose astatine readily, and care in this regard must be exercised when isolation from the target utilizes the wet method.

Although there is no way at present to decide whether the complex extracted is $AtCl_2^-$ or $AtCl_4^-$, it will be referred to in subsequent discussion as $AtCl_2^-$, and solutions obtained from it will be designated as containing compounds of At(I). None of the results reported are inconsistent with this assignment.

Reactions of astatine with phenol and benzene. The astatine activity can be removed quantitatively from the ether by shaking with a solution of NaOH, it only being necessary to have sufficient base so that all of the HCl dissolved in the ether is neutralized. Presumably the astatine is present as AtO^- in these solutions. The AtO^-, although probably unstable with respect to disproportionation, does not seem to decompose over the period of several hours. The low concentrations used (10^{-12} to 10^{-10} M), which could lead to a slow rate of reaction, probably account for this apparent stability.

A few observations have been made on solutions prepared by adding a small aliquot of the basic AtO^- solution to larger volumes of dilute sulphuric acid. These solutions, presumably containing HAtO, might be expected to react with organic compounds in a way similar to that of the other hypohalous acids. Two reactions were tested; the reaction with phenol, and the reaction with benzene. The first reaction was suggested by the reaction of HIO with phenol to yield iodophenols,[5] and the second by the reaction of benzene with HOBr in mineral acid media to give bromobenzene.[6] The possibility of these reactions was tested by shaking a portion

[4] D. E. Campbell, A. H. Laurene, and H. M Clark *J. Amer. chem. Soc.* **74**, 6193 (1952).
[5] V. Cofman *J. chem. Soc.* 1040 (1919); F. G. Soper and G. F. Smith *J. chem. Soc.* 2757 (1927).
[6] D. H. Derbyshire and W. A. Waters *J. chem. Soc.* 573 (1950).

of the acid solution with an equal volume of solvent for 2 min. The results are shown in Table 2. The solvent called CCl_4-phenol was a 10^{-3} M solution of phenol in CCl_4. The "washed" benzene was extracted six times with 4 M NaOH just prior to use.

TABLE 2.—REACTIONS OF HAtO WITH PHENOL AND BENZENE

Solution	Solvent	% of At in organic phase	% of At in organic phase that is back-extracted with 0·5 M NaOH
0·5 M H_2SO_4	CCl_4	16	—
0·5 M H_2SO_4	CCl_4-phenol	86	98
0·3 M H_2SO_4	CCl_4-phenol	76	95
0·5 M H_2SO_4	Benzene	88	23
0·3 M H_2SO_4	Benzene	91	36
0·3 M H_2SO_4	"Washed" benzene	54	—

It was found that after both the extraction with CCl_4-phenol and with benzene the astatine was in a form inert to the action of oxidizing and reducing agents that normally react with inorganic forms of astatine, suggesting that the astatine is now a part of an organic molecule. The results with phenol seem reasonably conclusive: the high percentage of back-extraction into base is consistent with the astatine being part of an acidic molecule such as an astatophenol. In the case of benzene it is difficult to decide whether the reaction is really with the benzene or is with some impurity in the benzene. Both the reaction with "washed" benzene, and the extent of back-extraction with base, indicate that phenol impurities cannot account for all the reaction.

Oxidation of At_2 with $S_2O_8^{=}$ is reported[1] to be slow at room temperature, but rapid at 50°. The oxidation state formed is unknown, but has been suggested to be astatate. Acid solutions of HAtO are apparently oxidized by hot $K_2S_2O_8$, since there is decreased reactivity with benzene. Results of treating AtO^- in 0·5 M H_2SO_4 with 0·1 M $K_2S_2O_8$ at 80° for 1 hour are:

Solvent	% of activity in organic phase	
	$S_2O_8^{=}$ treatment	no $S_2O_8^{=}$
"Washed" benzene	28	81
CCl_4-phenol	61	77

Reactivity with phenol still remains, but reactivity with benzene is reduced considerably. Regardless of what oxidation state is formed by the action of hot peroxydisulphate, this state is converted to an ether extractable chloro-complex when added to HCl solutions. Portions of the same oxidized solution used above were added to equal volumes of 12, 9, and 6 M HCl, allowed to stand 1 hour, and extracted with isopropyl ether in the same way as in earlier experiments.

Molarity, HCl	% extracted by ether
6	86
4·5	83
3	79

These percentages are all higher than those listed earlier for other methods of oxidation. However, in this last case the solution extracted is also 0·25 M in H_2SO_4, which may enhance the extraction. The other possibility is that a second chloro-complex, such as $AtCl_4^-$, is being formed.

Use of chloro-complex for isolation of astatine. The formation and ether extraction of the chloro-complex provides a convenient means of isolating astatine, either from the bismuth target or from the residues resulting from experiments. The treatments used in preparing solutions A, B, and C illustrate this point.

In making the isolation from the target, the bismuth is dissolved in nitric acid and the solution concentrated by boiling. The solution is not taken to dryness, as a little HNO_3 does not interfere. Concentrated HCl is added to bring the HCl concentration to 8 M, and the solution is cooled and extracted with the *iso*propyl ether. *Iso*propyl ether that has previously been equilibrated with 8 M HCl is somewhat better than pure ether for this purpose, since its use minimizes volume changes. The yields in a single extraction are better than 90%, the presence of Bi(III) salts increasing the extractability. Washing the ether phase with 8 M HCl removes about 10% of the activity. Less than 0·01% of the bismuth is retained in this procedure.

In the recovery of astatine from residues, all inorganic forms are converted to the complex; higher oxidation states by reduction with hydrochloric acid, lower oxidation states by oxidation with Cl_2. Organic forms are apparently not affected by this treatment. Because of the large amount of sodium compounds that appeared in the residues, sodium chloride often precipitated from the 8 M HCl solutions. Separation by centrifugation is satisfactory, as there is no tendency for the complex to be retained on the precipitate. Iron salts, if present, are oxidized to Fe(III) and are extracted along with the astatine. Back-extraction with NaOH solution precipitates $Fe(OH)_3$, which will carry some of the astatine. Only about 5% of the astatine is carried if the amount of $Fe(OH)_3$ is not exorbitant. The extraction procedure also serves to separate from Po^{211}, which accumulates from the decay of At^{211}.

DISCUSSION

The results obtained have been interpreted in terms of compounds of At(I) primarily because the reactions observed parallel those of iodine(I). An interpretation based on the (III) oxidation state might be as valid. Although the complex ICl_4^- is known, IO_2^- and HIO_2 are not known, so there is no guide to suggest how At(III) might behave.

Some attempts were made to separate the various oxidation states of astatine by paper chromatography and ionography, but these experiments were signally unsuccessful. Since it is unlikely that precipitation "carrier" studies will distinguish between the possible positive oxidation states, it now seems that the most promising method of studying these states is the utilization of differences in the organic reactions.

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THE EXTRACTION OF MERCURY(II) IODIDE*

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Abstract—The extraction of mercury(II) iodide into benzene at various acid and iodide concentrations was used as a means of determining the formation constants of the HgI_3^- and $HgI_4^=$ species. Radioactive tracer techniques were used to measure the extent of extraction at low mercury concentrations. With reasonable assumptions about activity coefficients the thermodynamic values of the constants for the formation of HgI_3^- and $HgI_4^=$ from HgI_2 and I^- were found to be $5{\cdot}0 \times 10^2$ and $5{\cdot}1 \times 10^5$, respectively.

THE equilibria which exist between mercury(II) iodide and iodide ion have been studied by using the extraction of the mercury species into benzene from dilute aqueous solutions as a phenomenon by which the extent of complex ion formation in the aqueous phase could be measured. A radioactive tracer, Hg^{203}, was used to determine the amount of extraction.

The application of an extraction technique to this equilibrium is not new,[1] but the use of a tracer permits the determination of lower concentrations of mercury and thus affords a worthwhile improvement in that the iodide ion concentration of the solution can easily be established. The amount of iodide undergoing combination can be neglected, since it is small compared to the total amount present.

EXPERIMENTAL

Solutions of nitric acid, potassium nitrate, and potassium iodide were prepared with reagent-grade chemicals and doubly-distilled water. A solution of mercury(II) nitrate containing radioactive Hg^{203} was obtained from the Oak Ridge National Laboratory. A standard solution of mercury(II) nitrate was prepared from this by precipitating the mercury as metal with hypophosphorous acid, weighing it, and dissolving it in concentrated nitric acid.

Distribution experiments were performed by shaking the aqueous solutions of mercury iodide with an equal volume of thiophene-free benzene for a period of about 12 hours at 25°C. The ratios of the concentrations of mercury in each phase were determined radiochemically. Aliquots from the equilibrated solutions were added to mercury(II) nitrate carrier, and the sulphide was precipitated and mounted for counting. Enough acetone was added to the benzene-mercury nitrate carrier mixture to make it one phase. After evaporation of the acetone and benzene, the sulphide was precipitated and mounted as mentioned above.

The distribution of mercury(II) between benzene and aqueous solutions was measured at an ionic strength of 0·03, nitric acid concentration of 0·01 M, and various potassium iodide concentrations in the range 0·001–0·02 M. Similar measurements were made with the nitric acid concentration being varied in the range 0·001–0·02 M, while the ionic strength was kept at 0·03 and the iodide ion concentration at 0·01 M. The total mercury present was in the range of 10^{-5} to 10^{-6} M and was always less than 1/300 of the total iodide concentration.

The distribution of mercury(II) iodide in the absence of excess iodide in the aqueous phase was measured by equilibrating a nearly saturated solution of HgI_2 in benzene (about 5×10^{-3} M) with a 0·01 M nitric acid–0·02 M potassium nitrate solution.

* Contribution No. 509. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

[1] M. S. SHERRILL *Z. physik. Chem.* **43**, 705 (1903).

RESULTS

The extraction ratio, E, was found to be invariant with hydrogen ion concentration in the range tested as shown in Table 1. This indicates that species such as $HHgI_3$ and H_2HgI_4 are not extracted into the benzene phase. It is reasonable to assume that mercury(II) iodide dissolved in benzene exists as HgI_2 molecules, since any ionization in this non-polar solvent is extremely unlikely.

TABLE 1.—THE DISTRIBUTION OF MERCURY(II) BETWEEN BENZENE AND 0·01 M KI SOLUTIONS OF VARYING HNO_3 CONCENTRATION

conc. HNO_3 (moles/litre)	E
0·001	0·39
0·006	0·37
0·010	0·39
0·020	0·38

The measurements of the distribution as a function of iodide concentration can be interpreted on the basis of the following equilibria in the aqueous phase.

$$HgI_2\,(aq) + I^- \underset{}{\overset{K_1}{\rightleftharpoons}} HgI_3^- \qquad (1)$$

$$HgI_2\,(aq) + 2I^- \underset{}{\overset{K_2}{\rightleftharpoons}} HgI_4^{=} \qquad (2)$$

An extraction ratio E and an extraction constant E^0 are defined as:

$$E = [HgI_2]_0/[Hg]_{tot,aq} \quad \text{and} \quad E^0 = [HgI_2]_0/[HgI_2]_{aq}.$$

Brackets denote concentrations in moles per litre. If equations (1) and (2) represent the prevailing reactions in the aqueous phase, then:

$$[Hg]_{tot,aq} = [HgI_2]_{aq} + [HgI_3^-] + [HgI_4^{=}]. \qquad (3)$$

This equation can be expressed in terms of the known iodide concentration, the concentration of mercury(II) iodide in benzene, the constants E^0, K_1, and K_2, and the activity coefficients of the ions I^-, HgI_3^-, and $HgI_4^{=}$, symbolized as γ_-, γ_1, and γ_2, respectively. The activity coefficient of uncharged mercuric iodide in the benzene phase at these concentrations is certainly close to unity, and it has been assumed to be that. In the aqueous-phase, calculations by LONG[2,3] indicate that at an ionic strength of 0·03, the deviation from unity for the activity coefficient of an uncharged species would be less than 0·5 per cent. This was considered to be negligible.

Thus:

$$[Hg]_{tot,aq} = \frac{[HgI_2]_0}{E^0}\left[1 + K_1[I^-]\frac{\gamma_-}{\gamma_1} + K_2[I^-]^2\frac{\gamma_-^2}{\gamma_2}\right]$$

or

$$\frac{1}{E} = \frac{1}{E^0}\left[1 + K_1[I^-]\frac{\gamma_-}{\gamma_1} + K_2[I^-]^2\frac{\gamma_-^2}{\gamma_2}\right] \qquad (4)$$

[2] W. F. MCDEVIT and F. A. LONG *J. Amer. chem. Soc.* **74**, 1090 (1952).
[3] F. A. LONG and R. L. BERGEN JR. *J. phys. Chem.* **58**, 166 (1954).

While it is possible to evaluate the constants in equation (4) with measurements in the presence of iodide, the errors involved make such evaluation quite inaccurate. Better estimates of K_1 and K_2 can be obtained by the use of the independent determination of E^0, in which a value of 47·2 was obtained for this constant.

The designation of this value as E^0 implies the assumption that aqueous mercury(II) iodide is not ionized in the concentration range of the experiment. Published measurements of the conductivity of mercury(II) iodide solutions[4] and the potentials of various couples involving mercury(II) iodide[5] indicate that it is largely in molecular form in aqueous solutions near the saturation point. The present measurement of E^0 was made with near-saturation conditions in both phases.

With the use of a measured value of E^0, equation (4) can be rearranged for better graphical interpretation into the form:

$$\frac{E_0 - E}{E[\mathrm{I}^-]} = \frac{K_1\gamma_-}{\gamma_1} + \frac{K_2\gamma_-^2\,[\mathrm{I}^-]}{\gamma_2} \qquad (5)$$

Experimental data expressed in this form as a function of iodide concentration are shown in Fig. 1. The satisfactory linearity of the plot justifies the use of equation (5) to interpret the data.

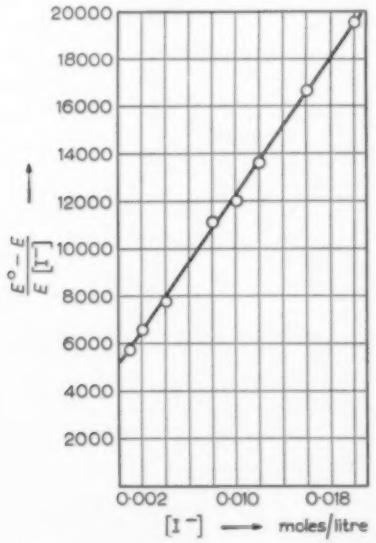

FIG. 1.—Mercuric iodide distribution study using benzene as extractant for HgI_2 0·0100 M HNO_3. $\mu = 0{\cdot}03$ (HNO_3, KNO_3, KI).

Values of $(5{\cdot}05 \pm 0{\cdot}12) \times 10^3$ and $(7{\cdot}24 \pm 0{\cdot}11) \times 10^5$ were determined for the intercept and slope of Fig. 1 by applying the method of least-squares for equally weighted measurements. Only the ordinate values were assumed liable to error. The above figures can be considered as nonthermodynamic values of K_1 and K_2 at an ionic strength of 0·03. They can be compared to the values of $(6{\cdot}1 \pm 2{\cdot}4) \times 10^3$ and

[4] F. KOHLRAUSCH and F. ROSE *Z. physik. Chem.* **12**, 241 (1893).
[5] I. QVARFORT and L. G. SILLÉN *Acta chem. scand.* **3**, 505 (1949).

$(10{\cdot}3 \pm 1{\cdot}1) \times 10^5$ which were determined by the use of electrometric measurements[5] in solutions of the same acidity and ionic strength.

For a calculation of the thermodynamic values of K_1 and K_2 some assumptions regarding the activity coefficients are necessary. The "effective diameter" of the I^- ion was estimated by KIELLAND[6] to be 3×10^{-8} cm. He also estimated values of 4×10^{-8} and $4{\cdot}5 \times 10^{-8}$ cm for the effective diameters of ions similar in type and size to HgI_3^- and $HgI_4^{=}$. By the use of these values and the Debye-Hückel expression:

$$-\log \gamma_i = \frac{AZ_i^2\mu^{1/2}}{1 + Ba_i\mu^{1/2}},$$

activity coefficients of 0·84, 0·85, and 0·52 were calculated for the I^-, HgI_3^-, and $HgI_4^{=}$ ions in these solutions, in which $\mu = 0{\cdot}03$. The ratios γ_-/γ_1 and γ^2_-/γ_2 were estimated to be 0·99 and 1·35, using the above values of the activity coefficients, and thermodynamic values of K_1 and K_2 equal to $(5{\cdot}1 \pm 0{\cdot}2) \times 10^3$ and $(5{\cdot}4 \pm 0{\cdot}2) \times 10^5$ were calculated.

[6] J. KIELLAND *J. Amer. chem. Soc.* **59**, 1675 (1937).

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THE CONCENTRATION OF PROTACTINIUM BY RE-CYCLING THROUGH AN ANION-EXCHANGE COLUMN

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Abstract—Protactinium was separated from major impurities by sorption on an anion-exchange resin from strong hydrochloric acid, followed by washing with the acid and elution with a mixture of hydrochloric and hydrofluoric acids. The gamma activity of the isotope (Pa^{231}) provided an adequate analytical procedure. Addition of either aluminium chloride or boric acid to the elution effluent rendered the protactinium resorbable by the resin. Re-elution of the protactinium with mineral acids was slow, but the re-employment of the hydrochloric acid-hydrofluoric acid elutriant produced a marked concentration of the product.

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THE various metals differ widely in their anion-exchange behaviour in hydrochloric acid solution.[1] This fact may be utilized in the purification of protactinium. Thus the latter, which is strongly sorbed by Dowex-1 resin from 9 N hydrochloric acid solution, is readily separated from the alkali and alkaline earth metals which exhibit no sorption. However, the similarity of some of the metals to protactinium in their sorption characteristics may render inconvenient their separation by simple hydrochloric acid elution. In any case, final elution of protactinium with hydrochloric acid may entail excessive dilution. Thus, MADDOCK and PUGH[2] separated protactinium and zirconium by this method, but recovered the protactinium only at the expense of a fourfold dilution. KRAUS and MOORE[3] showed that the separation of protactinium from iron by dilute hydrochloric acid elution is very slow, incomplete, and accompanied by great dilutions. They found, however, that if a mixed hydrochloric acid-hydrofluoric acid elutriant were used, a very sharp separation could be obtained, the protactinium being eluted quickly off the column. The iron was readily removed with dilute hydrochloric acid. The same authors[4] separated protactinium from niobium, tantalum, and zirconium, and more recently,[5] protactinium from thorium and uranium, by similar procedures.

The purification and concentration of protactinium by anion exchange, utilizing a mixed hydrochloric acid-hydrofluoric acid elutriant, may not always be accomplished in a single stage. One may thus be confronted with the problem of rendering the protactinium in the fluoride effluent resorbable by the resin. It was desired to add to the effluent some reagent which would form a stable fluoride complex, thus releasing protactinium from the complex fluoride ion and rendering the metal resorbable as a

* Mound Laboratory is operated by Monsanto Chemical Company for the United States Atomic Energy Commission under Contract No. AT-33-1-GEN-53.

(1) K. A. KRAUS and F. NELSON *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy* Vol. 7. pp. 113–125. United Nations, New York (1956).
(2) A. G. MADDOCK and W. PUGH *J. inorg. nucl. Chem.* **2**, 114 (1956).
(3) K. A. KRAUS and G. E. MOORE *J. Amer. chem. Soc.* **77**, 1383 (1955).
(4) K. A. KRAUS and G. E. MOORE *J. Amer. chem. Soc.* **73**, 2900 (1951).
(5) K. A. KRAUS, G. E. MOORE, and F. NELSON *J. Amer. chem. Soc.* **78**, 2692 (1956).

chloride complex. A soluble aluminium salt appeared attractive for this purpose, since aluminium forms stable complex fluorides.[6] Further, ELSON *et al.*[7] found that the addition of aluminium nitrate to a fluoride solution of protactinium made the latter extractable by di-*iso*butylcarbinol. GOLDEN and MADDOCK[8] reported similar results when they added the aluminium as the chloride and extracted with di-*iso*propyl ketone. A second additive which appeared attractive was boric acid, since it forms a very stable fluoborate ion.[9]

In the present work, after preliminary breakthrough tests, the protactinium in the feed solution was separated from its major impurities, iron and phosphorus, by sorption from strong hydrochloric acid solution, followed by washing with hydrochloric acid and eluting with the mixed hydrochloric acid-hydrofluoric acid elutriant. Phosphate ion would be expected to pass out of the column in the wash, since it has considerably less affinity for the resin than chloride ion.[10] Experiments were next conducted on the effectiveness of the additives in rendering the protactinium resorbable. Finally, the rate of re-elution of the protactinium with different mineral acids and with the hydrochloric acid-hydrofluoric acid mixture was studied.

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EXPERIMENTAL PROCEDURE

Column operation. The anion-exchange columns were made from 1- or 3-cm-diameter glass tubes into which Ace A frits were sealed. The resin was 100- to 200-mesh Dowex-1 X 10 in the chloride form. The columns were filled to the desired depth with a slurry of the resin. They were then prewashed with three column-volumes of hydrochloric acid whose normality equalled the acid normality of the feed. The effluent from each run was led through plastic tubing to glass vials in which successive fractions were collected. The vials were mounted in a circular drum which was rotated intermittently by a motor actuated by a timing mechanism. Flow rates were maintained at approximately 0·6 ml/min/cm^2 by means of a peristaltic pump.

Protactinium analysis. For the purpose of constructing breakthrough and elution curves, a knowledge of the concentration of the protactinium in the effluent fractions relative to its concentration in the feed was sufficient. Since the feed contained the element as the isotope of mass 231, its gamma spectrum provided a basis for an adequate analytical procedure. The spectrum showed characteristic peaks at 27, 95, and 300 keV.[11] Because the feed was essentially radiochemically pure, the counting rate at the 300 keV peak was found to be a suitable measure of the relative protactinium concentration. The total 300 keV count of the feed (obtained as the product of the counting rate of an aliquot and the appropriate volume ratio) was found to equal the sum of the 300 keV counting rates of the various effluents—provided fluoride elution was used to remove all protactinium from the column.

The gamma counter employed a single-channel pulse-height analyser with a 2 in. thallium-activated, sodium iodide well crystal. By adopting a standard vial and a fixed volume of liquid (approximately 2·5 ml) for the counting samples, the influence of geometry factors was eliminated. Direct utilization of liquid effluents as counting samples eliminated the labour of slide preparation required for alpha counting.

The use of the 27 keV-peak gamma counting rate instead of the 300 keV peak counting rate increased the precision of the measurement of the relative protactinium concentration, as judged by the reduced scatter of points about breakthrough and elution curves, but reduced the accuracy of this measurement, as judged by the greater discrepancy in the activity balance. The increased precision is attributable to the higher counting rate at the 27 keV peak, the reduced accuracy to the greater

(6) N. V. SIDGWICK *The Chemical Elements and Their Compounds* Vol. 1. p. 435. Clarendon Press, Oxford (1950).
(7) R. ELSON, G. W. MASON, D. F. PEPPARD, P. A. SELLERS, and M. H. STUDIER *J. Amer. chem. Soc.* **73**, 4974 (1951).
(8) J. GOLDEN and A. G. MADDOCK *J. inorg. nucl. Chem.* **2**, 46 (1956).
(9) N. V. SIDGWICK *Ibid.* **1**, 409 (1956).
(10) R. M. WHEATON and W. C. BAUMAN *Industr. engng. Chem.* **43**, 1088 (1951).
(11) M. L. SALUTSKY, K. SHAVER, A. ELMLINGER, and M. L. CURTIS *J. inorg. nucl. Chem.* **3**, 289 (1956).

sensitivity of the counting rate at 27 keV to absorption of gamma energy by inert solutes. Unless otherwise stated, the elution and breakthrough curves were based on the gamma counting rate at the 300 keV peak.

Preparation of feed solution. The feed solution used in these experiments was prepared from a residue obtained in the processing of uranium minerals. The solution was made by dissolving the residue in hydrochloric acid, salting out the protactinium on a carrier, redissolving the washed carrier in hydrochloric acid containing a small amount of sulphuric acid, and further concentrating the protactinium by extraction with di-*iso*butylcarbinol and final stripping with water. The strip solution was approximately 4·5 N in acid, and contained only a trace of sulphate ion. To convert the solution into a suitable anion-exchange column feed, concentrated hydrochloric acid was added until the acidity became 9 N.

Feed solutions prepared in this way contained essentially radiochemically pure protactinium-231 as judged by their gamma spectra. Alpha counting gave a protactinium content of 4·1 μg/ml. The total solid content was found to be 0·040 g/ml, making the protactinium concentration about 1 part in 10,000 on a dry basis.

The feed solution was deeply coloured by iron. A semiquantitative spectroscopic analysis by the Harvey method showed that, in addition to chloride ion, the elements listed in Table 1 were present.

RESULTS AND DISCUSSION

Breakthrough tests and radiochemical purity. A breakthrough test was made with the feed solution, using a resin bed, 1 cm in diameter and 2 cm long. The counting rate of the effluent relative to that of the feed is plotted against accumulated effluent volume in Fig. 1. After correcting for holdup, the breakthrough point, taken as the point at which the relative concentration reached 0·04, was 4 ml. A value twice this large was obtained in a run in which the bed-depth was doubled, thus confirming the linear relation between breakthrough capacity and column length.

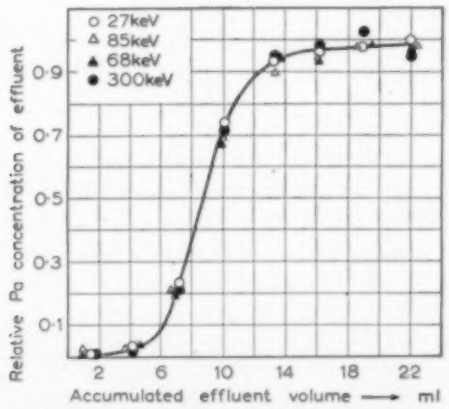

FIG. 1.—Breakthrough curve for radiochemically pure feed solution based on gamma counting rate at different energy levels.

The gamma activity of the residue from which the feed solution was prepared had indicated the presence of thorium-230 and radium-223. These isotopes exhibit peaks in their gamma spectra in the neighbourhood of 68 keV and 85 keV, respectively.[12] However, as is evident from Fig. 1, in the breakthrough test with the feed solution, the counting rates at 27, 68, 85, and 300 keV all gave practically identical breakthrough curves, and this continued to be true when the bed-depth was doubled. Since thorium

[12] Nuclear Data *NBS Circular* 499, pp. 256, 261 (1950)

and radium are not sorbed by the resin from hydrochloric acid solution,[1] one can conclude that the feed solution is essentially free of thorium-230 and radium-223.

For comparison, the results of a breakthrough test with a radiochemically impure feed are given in Fig. 2. This feed was made by merely prewashing the carrier in versene prior to solution in hydrochloric acid, thus eliminating extraction with di-*iso*-butycarbinol. The acid concentration of the solution was again 9 N and the resin bed

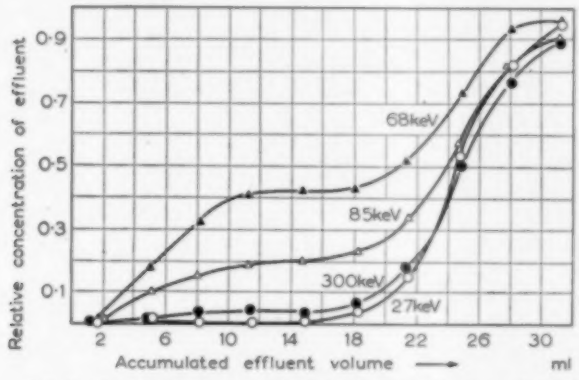

FIG. 2.—Breakthrough curves for radiochemically impure solution based on gamma counting rate at different energy levels.

1 cm in diameter and 2 cm long. However, the iron and protactinium concentrations were considerably lower. Particularly noteworthy is the fact that the four curves, based on the counting rates at the four different energy levels, were no longer identical. The 27 keV curve showed a breakthrough point at 17 ml of effluent. The 85 keV curve rose rapidly during the initial effluent fractions, levelled off at a relative concentration of 0·20, and then resumed its rise at the 27 keV breakthrough point. The 68 keV curve was similar to the 85 keV curve, except that the temporary flat in the curve came at a relative concentration of 0·42. The 68, 85, and 300 keV curves appeared to approach unity asymptotically, with the 27 keV curve exceeding that value somewhat. The results indicate that 20 per cent of the 85 keV counting rate, and 42 per cent of the 68 keV counting rate of the feed are attributable to radium-223 and thorium-230. The existence of a 285 keV peak in the radium spectrum may explain the appearance in the 300 keV curve of a temporary flat at a relative concentration of 0·04. No further use was made of this feed solution in the experiments to be described.

Purification by sorption from hydrochloric acid solution followed by fluoride elution. A column, 1 cm in diameter and 8 cm deep, was charged with 8 ml of feed solution (50 per cent of breakthrough capacity). After washing with 31 ml of 9 N hydrochloric acid, the column was eluted with 50 ml of an acid solution which was 7 N in hydrochloric acid and 0·05 N in hydrofluoric acid. The column was finally stripped with 1 N hydrochloric acid. The protactinium concentrations of successive effluent fractions, relative to the feed, are plotted against accumulated effluent volume in Fig. 3. The strip solution, which contained the bulk of the iron, is not included, since its activity was negligible. The 27 keV curve followed closely the 300 keV curve except in the peak region, where the former rose above the latter. The total 27 keV gamma count recovered in all of the effluents was 111·6 per cent of the feed, whereas the total

300 keV count was 99·7 per cent of the feed. The unexpected breakthrough during sorption and washing amounted to 5 per cent of the feed activity. Relative counting rates at 27, 68, 85, and 300 keV indicated that these breakthrough effluents contained protactinium rather than thorium or radium. However, since the percentage breakthrough loss remained the same when the quantity of feed was halved, it appeared that a small fraction of the protactinium in the feed had assumed a form not sorbable by the resin.

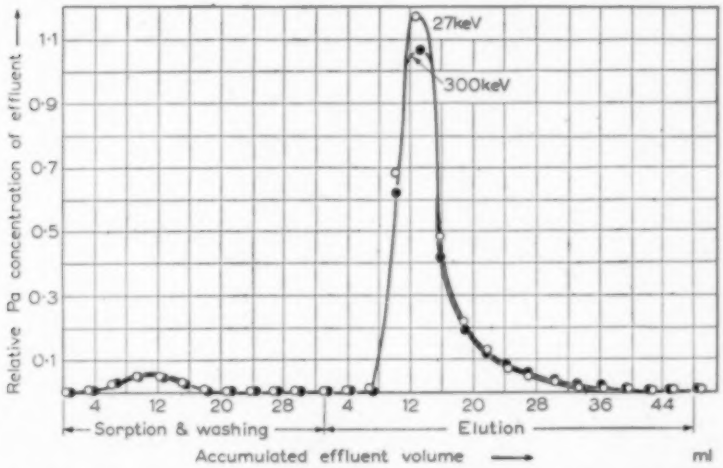

FIG. 3.—Concentration of protactinium in effluent, relative to feed concentration, during sorption, washing, and fluoride elution. (Feed: 8 ml; Wash: 31 ml 9 N HCl; Elutriant: 7 N HCl + 0·05 N HF.)

The above run was scaled-up ninefold by increasing the bed diameter to 3 cm and the quantities of solutions and the flow-rate correspondingly. The gamma activity of the effluent fractions agreed well with Fig. 3 for the smaller-scale run. The protactinium-rich elution effluents were pooled to give a solution containing 91 per cent (96 per cent, if we ignore the 5 per cent breakthrough) of the 300 keV activity present in the feed. The volume of this solution was 1·88 times that of the feed solution. Additional runs, in which the quantity of feed and the elutriant concentration were varied, were unsuccessful in avoiding this dilution. The amount of dry solids present was reduced by a factor of 41·4 from the amount present in the feed. The results of spectroscopic analysis, presented in the last column of Table 1, showed that the ion-exchange procedure was successful in separating the protactinium from the iron and phosphorus, although niobium and titanium were only partially removed. The action of the hydrofluoric acid on the glass is the likely cause of significant amounts of boron, zirconium, calcium, and sodium, which were also reported in the elution effluent.

Effect of additives on resorption of protactinium from fluoride solution. The pooled elution effluent, prepared as described, was treated with concentrated hydrochloric acid until the acid normality was increased to approximately 9 N, thus reducing the hydrofluoric acid concentration to 0·03 N. The resulting solution was employed as feed in experiments devoted to the effect of additives on resorption of protactinium from fluoride solution. These experiments employed resin beds 1 cm in diameter and

4 cm deep, pretreated in the usual way with hydrochloric acid. In the control experiment, 25 ml of the feed was run onto the column followed by 40 ml of 9 N hydrochloric acid wash. In two other experiments the feed was made 0·1 M in aluminium chloride and boric acid, respectively, and the procedure repeated.

TABLE 1.—SPECTROSCOPIC ANALYSIS OF FEED AND ELUTION EFFLUENT
(Micrograms of constituent per milligram of evaporated feed)

Element	Feed	Elution Effluent
P	400	0
Fe	340	0·25
Nb	40	14
Ti	25	3
Mn	2	0·02
Si	1	0·75
Al	0·5	2
Ni	0·4	0·02
Cu	0·1	0·01
Mg	0·1	0·02

In Fig. 4 the accumulated per cent protactinium in the effluent, as based on the 300 keV counting rate, is plotted against accumulated effluent volume for the three runs. The control run showed protactinium breaking through rapidly and levelling off during the washing at 84 per cent of the charge. Both additives, however, were successful in rendering the protactinium sorbable by the resin, thus completely

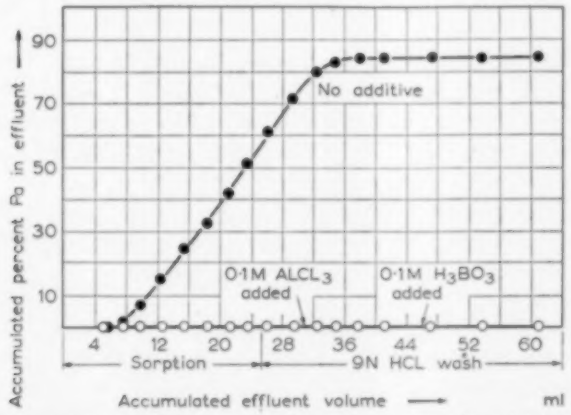

FIG. 4.—Effect of additive on resorption of protactinium from fluoride effluent.

suppressing the breakthrough. The quantity of wash used was sufficient to eliminate excess aluminium from the column, since the later wash-effluents responded negatively to alizarin tests. Similarly, in the run employing the boric acid-treated feed, the later wash effluents gave no test for borate with curcuma paper. Finally, the zirconium-alizarin test indicated that the washing practice was sufficient for removal of excess fluoride.

Re-elution with hydrochloric acid. Having established that protactinium might be

resorbed from a fluoride solution, provided a suitable additive was employed, the rate of re-elution with hydrochloric acid was next explored. In each experiment, 25 ml of the boric acid-treated fluoride effluent, prepared as described above, was fed onto a column 1 cm in diameter and 4 cm long, followed by 40 ml of 9 N hydrochloric acid wash. The column was then eluted with dilute hydrochloric acid. Fig. 5 gives the integral elution curves obtained with various concentrations of hydrochloric acid elutriant. When water was used, the curve levelled off quickly at 14 per cent of the charge, doubtless because of hydrolytic trapping of protactinium in the resin. A

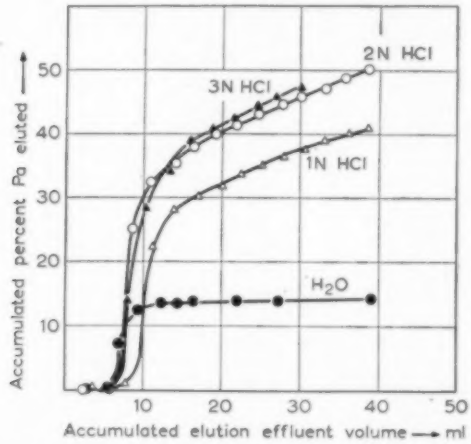

FIG. 5.—Re-elution of protactinium with hydrochloric acid. (Feed: 25 ml of boric acid-treated fluoride effluent. Wash: 40 ml of 9 N HCl.)

marked improvement in elution rate was obtained with 1 N hydrochloric acid. A smaller additional increase was observed when 2-normal acid was used. However, even in the latter case, the elution was prohibitively slow since, at 40 ml of effluent, approximately half of the protactinium still remained on the column and was being eluted at the rate of only about one-half per cent per millilitre. Furthermore, the fact that the curve for 3 N acid was nearly identical to that for the 2 N acid indicated that further improvements in elution rate with increasing acid concentration could not be expected, presumably because of the increasing tendency for sorption of protactinium as a chloride complex.

Several of the effluents obtained with the 1 N hydrochloric acid elutriant gave negative tests for fluoride with zirconium-alizarin paper. Weak borate tests were obtained with curcuma paper.

Re-elution with different mineral acids. Fig. 6 compares the elution rates obtained with different mineral acids, each at 3 N concentration. The experimental procedure prior to elution was the same as that followed in the preceding section. The differences between the elution rates obtained with the three acids were not marked. The hydrochloric acid curve showed superior initial elution rates, but crossed the sulphuric acid curve at about 35 ml of effluent. The nitric acid curve paralleled that obtained with hydrochloric acid, but remained consistently below it.

Effect of quantity of feed on rate of re-elution. A series of runs was made in which varying quantities of the boric acid-treated feed were charged on to the column. The

column dimensions and washing procedure were the same as before. The elutriant was 2 N hydrochloric acid. The integral elution curves of Fig. 7 show that the elution rate was improved as the quantity of feed was increased from 15 ml through 25 ml to

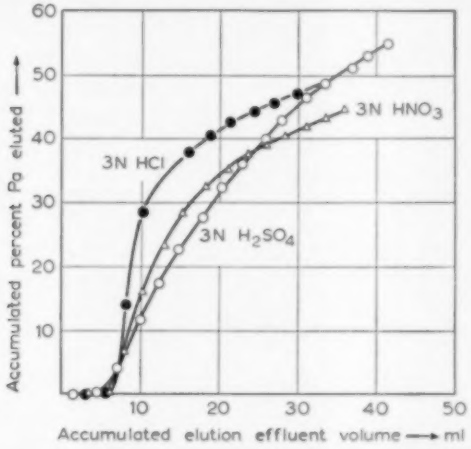

FIG. 6.—Re-elution of protactinium with different mineral acids. (Feed: 25 ml boric acid-treated fluoride effluent. Wash: 40 ml 9 N HCl.)

40 ml, but nevertheless remained unsatisfactorily low. Also, a further increase to 100 ml of feed caused a marked drop in elution rate. It should be noted that no protactinium breakthrough occurred during sorption and washing, even with this large quantity of feed.

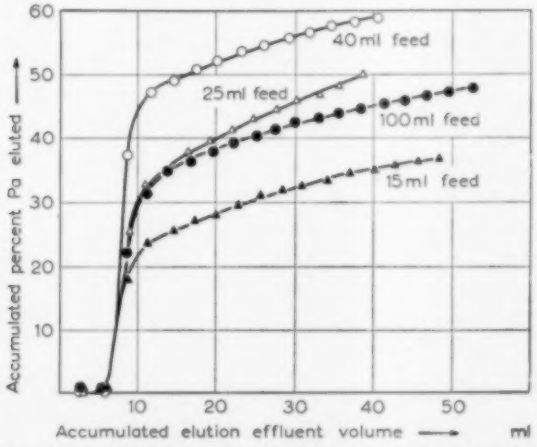

FIG. 7.—Effect of quantity of feed on rate of re-elution of protactinium with 2 N hydrochloric acid. (Feed: boric acid-treated fluoride effluent. Wash: 40 ml 9 N hydrochloric acid.)

Concentration of protactinium by re-elution with fluoride solution. The experiments described indicated that, after resorption from a boric acid-treated fluoride effluent, protactinium could not be re-eluted with mineral acids without excessive dilution. It was of interest to determine what concentration might be obtained by re-elution with

fluoride solution. As before, a 1 × 4 cm column was charged with the boric acid-treated fluoride effluent, 9 N in hydrochloric acid and 0·03 N in hydrofluoric acid, but feeding was now continued to 140 ml. Monitoring of the effluent indicated that no breakthrough had occurred; however, the formation of gas-bubbles in the resin precluded continuation of the sorption process. The great increase in breakthrough capacity, as compared with the original feed prior to iron and phosphorus removal, is attributed to the low iron content. The latter forms a tight band extending from the top of the column and tends to force protactinium into the effluent.

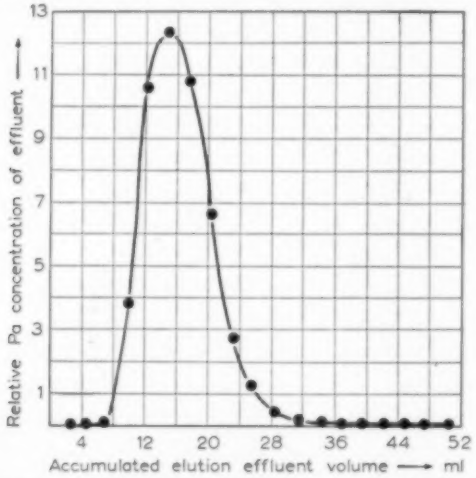

FIG. 8.—Concentration of protactinium in effluent, relative to feed concentration, during fluoride re-elution. (Feed: 140 ml boric acid-treated fluoride effluent. Wash: none; elutriant: 9 N HCl + 0·1 N HF.)

Without washing, the column was eluted with a solution 9 N in hydrochloric acid and 0·1 N in hydrofluoric acid. The high hydrochloric acid concentration, even though it doubtless reduced the protactinium concentration of the effluent, was deemed desirable for the purpose of retaining on the column those metal chloride complexes unaffected by the fluoride ion. The differential elution curve is given in Fig. 8. The protactinium concentration rose quickly to a peak value of over twelve times that of the feed, then dropped rapidly with little tailing. The activity balance, based on the 300 keV peak counting rate, showed only a 93 per cent recovery of protactinium in the effluent. The discrepancy is attributable to the more concentrated effluent fractions which exhibited counting rates approaching the upper limit for reliable counter performance. Approximately 98 per cent of the protactinium eluted was contained in an effluent volume equal to only 13 per cent of the feed volume. This is in marked contrast to the initial purification step, where dilution factors of the order of 2 were obtained.

This experiment demonstrates the feasibility of concentrating protactinium by recycling the boric-acid treated fluoride effluent on to the anion-exchange column and subsequently re-eluting with the hydrofluoric acid-hydrochloric acid mixture.

Acknowledgement—The author is indebted to Dr. L. V. JONES for preparation of the feed solution, to Mr. H. W. KIRBY for its analysis by alpha counting, and to Mr. J. M. GOODE for the spectroscopic analysis.

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LETTERS TO THE EDITORS

On the half-life of O^{20}

(*Received* 11 *February* 1957)

THE potential utility of a radioactive isotope of oxygen with a half-life longer than that of O^{15} (2 min) stimulated a search for O^{20}.[1] This search showed that the half-life of O^{20} is not in the range 10 min to 150 years.

Recently calculations have been made here on the binding energies of light nuclei;[2] these have provided an estimate of the mass of O^{20}, from which a probable value for the half-life can be deduced.

The binding energy of F^{20} and the mass difference between the proton and the neutron have been determined by experiment;[3] if we assume the binding energy of O^{20} to be that previously calculated,[2] we obtain $3{\cdot}9 \pm 0{\cdot}9$ MeV for the disintegration energy of O^{20}. As has been already noted,[1] the predominant decay of O^{20} is probably not to the ground state but to the first excited state, 0·65 MeV, or another near lying level. Probably one of these low excited levels has $J = 1$, and belongs to the configuration $d^4_{5/2}$; the decay from the ground state of O^{20} to this level will then be allowed. It is reasonable to assume that the log ft value in the case of O^{20} will be close to that of the decay of F^{20} to the excited level of Ne^{20}; this latter value is 4·88. Taking, in our case, log ft = 5, we get a half-life of $3(^{+8}_{-2})$ min. It seems, therefore, that the potential utility of this isotope is somewhat doubtful. We wish to thank Dr. SAMUEL for pointing out to us this problem.

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[1] S. KATCOFF and J. HUDIS *J. inorg. nucl. Chem.* **3**, 253 (1956).
[2] I. TALMI and R. THIEBERGER *Phys. Rev.* **103**, 718 (1956).
[3] A. H. WAPSTRA *Physica* **21**, 367 (1955).

The displacement of atoms in polonium and its compounds by radioactive decay

(*Received* 15 *March* 1957)

POLONIUM-210 emits 10^{13} alpha particles/min/mg. It is the purpose of this note to calculate the number of atoms likely to be displaced from their normal lattice sites by collision with alpha particles or recoiling nuclei.

The number, N_d, of atoms displaced by hard-sphere collisions with a moving atom of energy E can be estimated from the equation $N_d = E/2E_d$.[1] This equation is valid only when $E > 2E_d$, where E_d is the energy needed to displace an atom from its lattice site, but less than a certain value, L_d, above which the hard-sphere approximation does not hold. KINCHIN and PEASE[1] suggest that as the displacement energy, E_d, varies with the direction of recoil and with the nature of the substance

[1] G. M. KINCHIN and R. S. PEASE *Progress in Physics* **18**, 1 (1955).

studied, and is also very difficult to calculate, the isotropic value of 25 eV can be used in most calculations, as first suggested by SEITZ.[2] The value of L_A can be derived from the equation:

$$L_A = 2E_R Z_1 Z_2 (Z_1^{2/3} + Z_2^{2/3})^{1/2}(M_1 + M_2)/M_2,$$

where E_R is the Rydberg energy (13·60 eV), Z and M are atomic numbers and masses respectively, and the subscripts 1 and 2 refer to moving and stationary atoms respectively.

For polonium, the energy of the recoiling heavy nucleus (100 keV) is below the upper energy limit, L_A, for hard-sphere collisions, but well above the displacement energy E_d. The number of atoms displaced by the recoiling heavy nucleus can therefore be calculated from the above equation to be 2000.

The energy of the alpha particle (5·4 MeV) is well above the upper energy limit for hard-sphere collisions, and therefore the number of atoms displaced by the alpha particle cannot be calculated from the equation given above. SEITZ[2] calculates that 59 atoms are displaced per alpha particle in germanium by bombardment with 5 MeV alpha particles. The minimum alpha-particle radiation energy to produce a displaced atom in germanium is about 100 eV, whereas the energy necessary to produce a displaced atom in polonium is about 300 eV. On this basis, the number of atoms displaced in polonium by a 5·4 MeV alpha particle would be less than 59. As we are concerned primarily with orders of magnitude, we can neglect the number of atoms displaced by collision with alpha particles in polonium as compared to the displacements caused by the recoiling nucleus.

KINCHIN and PEASE[1] calculate that 2000 atoms are displaced, mainly by the recoiling heavy nucleus, for every alpha disintegration of uranium in various radioactive minerals. The alpha-particle and recoil energies for uranium are respectively 4·2 MeV and 100 keV. As these energies are comparable with those for polonium, we would expect the number of displaced atoms for each alpha disintegration of uranium to be approximately the same as the number displaced in polonium. The calculations outlined above suggest that this is the case. However, as the physical assumptions in the derivation of the formula $N_d = E/2E_d$ are such that it probably represents an overestimate of the number of displaced atoms, the value of 1000 displaced atoms per alpha disintegration is used in the following discussion.

Therefore, in 1 mg of polonium (10^{13} disintegration/min/mg), 2×10^{19} atoms are knocked off their lattice sites per day. However, as there are only 3×10^{18} atoms in 1 mg of polonium, each atom will be displaced at least once a day. The number of atoms in a milligram of PoO_2, $PoBr_4$, $PoCl_4$, etc., is also of the order 10^{19}. Similarly then, in these compounds each atom will be displaced at least once a day.

The diffraction pattern of polonium tetrabromide was indexed on the basis of a face-centred cubic cell.[3] On spatial considerations, the cell could only contain one molecule of $PoBr_4$, and hence one atom of polonium. However, the face-centred cubic space groups, which contain no one- or twofold symmetry positions, require a minimum of four polonium atoms per unit cell, which is not possible on spatial considerations. In order to correlate the diffraction data with the chemical analytical data for $PoBr_4$, two suggestions were made:[3] (1) the true cell was of lower symmetry and that the lines due to the true cell were extremely weak and not observed on the diffraction photograph, and (2) that the cubic cell contains one molecule of $PoBr_4$ with the one polonium atom randomly distributed over the sites which would normally be occupied by four cations. With this statistical distribution of polonium atoms the face-centred cubic symmetry would be preserved. Intensity calculations and interatomic distance considerations were not incompatible with the second suggestion. Further weight is now added to this suggestion of random distribution by the calculation showing that an hour after preparation, 10^{18} atoms have been displaced from their lattice sites. Thus, as there are only 6×10^{18} atoms in a mg of $PoBr_4$, the structure can be considered to be highly disordered even 1 hour after preparation.

The phase transitions observed when polonium[4] and polonium oxide[5] are aged for a week might well be a function of radiation damage, an ordered going to a disordered state, and not, as suggested previously, a function of temperature. Further work is needed to confirm this suggestion.

We have found that X-ray powder diffraction photographs of polonium compounds which are a few days old are of poorer quality than the photographs of the freshly prepared samples. In view

[2] F. SEITZ *Disc. Faraday Soc.* **5**, 271 (1949).
[3] K. W. BAGNALL, R. W. M. D'EYE, and J. H. FREEMAN *J. chem. Soc.* 3959 (1955).
[4] W. H. BEAMER and C. R. MAXWELL *J. chem. Phys.* **17**, 1293 (1949).
[5] K. W. BAGNALL and R. W. M. D'EYE *J. chem. Soc.* 4295 (1954).

of the above calculation, this would be expected. Further, after about 3 weeks, when every atom has been displaced at least twenty times, the X-ray diffraction photographs show the substance has become amorphous. This is analogous to the transformation to the metamict state of some minerals containing uranium or thorium. The metamict state is defined as the amorphous end-product of prolonged irradiation. According to HURLEY and FAIRBAIRN,[6] photographs of the mineral zircon become immeasurable after a radiation dose of 6×10^{15} alpha particles per mg. KINCHIN and PEASE[1] suggest that the saturation dose for a number of compounds studied is of the order 10^{-3} bombarding particles per atom (BPPA). So far, our results indicate that polonium and some of its compounds do not transform to the metamict state until a dose of 3×10^{17} alpha particles or 0·2 BPPA has been reached.

The reason why substances transform to the metamict state is still uncertain. According to KINCHIN and PEASE,[1] the displacement of atoms to interstitial sites does not in itself produce this state. They suggest the following mechanisms by which disorder can be produced: (1) the structure becoming unstable at interstitial concentrations of less than the saturation value, (2) atoms going to the wrong type of lattice site, (3) the disarrangement of relatively large volumes of material in a single event, and (4) the accumulation of impurities. With polonium and its compounds it is difficult to follow the build-up of "damage," and hence determine by which mechanism the metamict state is produced, as the number of displacements per day is too great. However, by preparing tellurium compounds containing small amounts of polonium we should be able to control the number of displaced atoms and then be able to follow the build-up of "damage."

I should like to thank Dr. R. A. DUGDALE for valuable discussion.

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Note added by I. F. Ferguson

A novel possibilty arises from the above calculations on the number of atoms displaced per day in Po^{210}. The structure of an element and its compounds might well depend upon the isotopic composition of the element and hence its rate and mode of radioactive disintegration. For example, the structure of Cm^{242} and its compounds, an alpha emitter of 162 day half-life, might well differ from that of Cm^{244}, an alpha emitter of 19·2 years half-life.

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[6] P. M. HURLEY and H. W. FAIRBAIRN *J. appl. Phys.* **23**, 1408 (1952).

Screening constants derived from atomic term distances as function of the ionic charge

(*Received* 4 *December* 1956)

HEISENBERG (ref. 1, p. 300) and CADY (ref. 1, p. 203) reported that the distances between multiplet terms are very nearly a linear function of the ionic charge for identical configurations of an isoelectronic series. In the theory of SLATER,[1] these term distances are expressed as multiples of the integrals F^k, which represent the repulsion energy between electrons within the same shell, and which are inversely proportional to the average radius of isomorphous radial functions of the partly filled shell. The dependence of F^k on the ionic charge is determined only by geometrical quantities,[2] while the energy differences between different shells (also the ionization potentials), or the Landé multiplet splitting[3] factors ζ_{nl}, are functions also of the electric potential in the kernel. SLATER[4] proposed effective charges $Z_\bullet$ smaller than the atomic number Z and larger than Z_0, the ionic charge plus 1. It was especially the ionization potentials which were described by this method, while the concept of

[1] E. U. CONDON and G. H. SHORTLEY *Theory of Atomic Spectra* (Second Edition) Cambridge (1953).
[2] C. KLIXBÜLL JØRGENSEN *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.* **30**, No. 22 (1956).
[3] C. KLIXBÜLL JØRGENSEN *J. inorg. nucl. Chem.* **1**, 301 (1956).
[4] J. C. SLATER *Phys. Rev.* **36**, 57 (1930).

screening constants $Z - Z_s$ is not advantageous in the treatment of ζ_{nl}, which is more dependent[5] on Z_0.

The present note is an attempt to define Z_s from the almost linear dependence of term distances on Z_0. The diagram gives the distances between the baricentres* of the terms of partly filled p-shell.[5] It is obvious to extrapolate the straight lines to zero and thus to assume the term distances proportional to $Z_0 + Z_c$. The values of Z_c turn out to be:

$2s^22p^2$	1·0	$3s^23p^2$	1·6
$2s^22p^3$	1·5	$3s^23p^3$	2·3
$2s^22p^4$	2·1	$3s^23p^4$	3·0

while the similar values for partly filled $4p$-shells seem to increase from 2·3 to above 3. Even though the slopes of the lines between $Z_0 = 1$ and 2 often are 5 to 10% larger than the slope for larger Z_0, the conspicuous linearity suggests approximately isomorphous radial functions with a certain amount

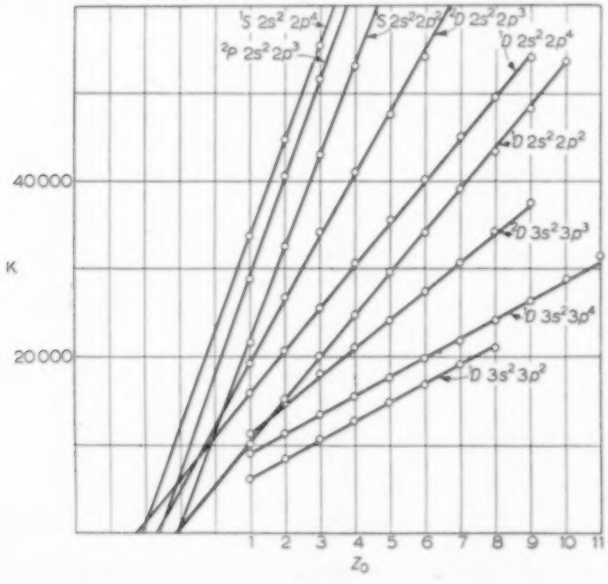

FIG. 1.

of screening, represented by Z_c. With SLATER,[4] it might be proposed to attribute this screening to the s-electrons. However, HARTREE's self-consistent radial functions do not have much smaller values of r_{max} for ns- than for np-electrons, and the energy difference between $2s$- and $2p$-electrons is only from 35% (Be) to 11% (O^{+4}) of the ionization potential in the series $2s^22p^3$. It may be more reasonable to consider Z_c as a property of the whole electron configuration. The highly excited configurations $2p^2$ and $2p^3$ without $2s$-electrons have ill-defined values of Z_c between $-1{\cdot}6$ and $+0{\cdot}4$. It is interesting that the linearity in Z_0 still holds, even though the ratios 6 : 9 for the distances $^3P : {}^1D : {}^1S$ for p^2 and p^4 and 9 : 6 for the distances $^4S : {}^2D : {}^2P$ for p^3 (also with s^2), are very distorted for the $2p$-shell.[1] RACAH[6] supposes that these deviations† are caused by intermixing between the configurations

* I.e. the average of the energy levels of the terms, when weighted by their degeneracy numbers.[7] It is often denoted the "centre of gravity," but does not involve a multiplication by the deviations from the mean.

† Even though the interaction between the two ^1D of $3p^2$ and $3s3d$ in Mg has been much discussed (ref. 1, p. 366), these two levels seem to have as low a distance as 267K in Si^{+2}.

[5] C. E. MOORE *Atomic Energy Levels. Nat. Bur. Stand. Circular No.* 467, Vols. I and II.

[6] G. RACAH *Proc. Rydberg Centennial Conference on Atomic Spectroscopy* Lund p. 31. (1954) (in *Lunds Universitets Årsskrift* N.F. 50 (1954) No. 21)

$2s^22p^n$ and $2p^{n+2}$. However, ^1D of $2p^2$ is also distinctly too low, which may be explained by the correction energy $\propto L(L+1)$ according to TREES.[6] It is remarkable that the partly filled $3p$-, $4p$-, $5p$-, and $6p$-shells are not influenced by similar strong deviations* from the simple theory as is the $2p$-shell. The absolute magnitude of the integral F^2 is $(Z_0 + Z_s)18{,}000K$ ($= \mathrm{cm}^{-1}$) for $2s^22p^n$, while it is decreased to $(Z_0 + Z_s)9{,}000K$ for $3s^23p^n$ and has similar values for the neutral atoms of all the following p-shells.[1] The development corresponds to the increased average[12] radius r_0 of the $3p$-shell, compared to the $2p$-shell. It compares favourably[12] with the magnitude $Z_0 \cdot 27400K$ of $\frac{1}{2}$W for a hydrogen-like $2p$-electron.

In the first transition group, RACAH[4] investigated the distance between P and F-terms with maximum value of S in the configurations $3d^n4s^2$ with $Z_0 = q + 1$, and observed fine agreement with the wavenumber

$$2679 + 3158q - 111q^2 + 853n + 2187k$$

If the term q^2 is neglected, $Z_s = -0{\cdot}15 + 0{\cdot}27n + 0{\cdot}69k$. Thus, the screening effect of a $4s$-electron is very small, amounting to only 0·31 of the effective charge. This is of chemical interest, since ORGEL[7] emphasized the analogy between the decreased F^2-integrals in complexes and in gaseous $3d^n4s^2$-ions, compared to gaseous $3d^n$-ions. However, this effect ~15% decrease can explain at most the behaviour of weakly covalent complexes, e.g. of divalent manganese, while the trivalent metals must have the partly filled d-shells intermixed with the orbitals of the ligands.[2,12,13] The reciprocal screening of d-electrons is rather large, ~0·73 according to RACAH's results.

As already pointed out by CADY,[1] the F^2-integrals are ~80% larger than predicted for hydrogen-like $3d$-electrons, even when they are approximately proportional to Z_0, as is the case for $3d$.[5] Recently, HARTREE[8] has reported self-consistent d-radial functions, which clearly demonstrate the the deviations from the hydrogen-like form. This behaviour is connected with the potentials, corresponding to Z near the nucleus and Z_0 for large distances from the nucleus. However, the average radii are shown to be inversely proportional to the F^2 integrals, as expected of those nearly isomorphous functions. The evidence presented in this note supports strongly an analogous development for most partly filled shells. It is remarkable how equal the slopes of the energies as function of Z_0 are for "Mirror" configurations p^2 and p^4 and how constant the proportionality between F^2 and $Z_0 + Z_s$ is for all configurations of a given np-shell.

In the case of f-electrons, a similar proportionality of term distances to $Z_0 + 1$ has been reported by the present author[9] for Np(III) and Pu(IV) and other cases, while BUTEMENT[10] compared the pairs Sm(II) : Eu(III) and Eu(II) : Gd(III), of which Z_s seems to be between 2 and 3. Finally, the increase of F^2 from the f^3-system Pr(III) to the f^{12}-system Tm(III) suggests Z_s to increase ~0·18 for each f-electron for $Z_0 = 4$.

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* *Landolt-Börnstein Tables* 6. Auflage, I. Band, 1. Teil, p. 276 (1950).

[1] L. E. ORGEL *J. chem. Phys.* **23**, 1004 and 1824 (1955).
[2] D. R. HARTREE *J. opt. Soc. Amer.* **46**, 350 (1956).
[3] C. KLIXBÜLL JØRGENSEN *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.* **29** No. 7 and 11 (1955).
[4] F. D. S. BUTEMENT *Trans. Faraday Soc.* **44**, 617 (1948).
[5] C. KLIXBÜLL JØRGENSEN *Acta chem. scand.* **9**, 540 (1955).
[6] C. KLIXBÜLL JØRGENSEN *Acta chem. scand.* **9**, 1362 (1955); **10**, 500, 518, 887 (1956); **11**, 53, 73 (1957).
[7] C. KLIXBÜLL JØRGENSEN *Energy Levels of Complexes and Gaseous Ions* Gjellerup, Copenhagen (1957).

Possible hydrogen bonding in certain interactions of organic phosphorus compounds*

(*Received* 19 *March* 1957)

IN A study of the extraction of trivalent lanthanides and americium from an aqueous mineral acid phase into a toluene solution of di(2-ethyl hexyl) orthophosphoric acid, $[(C_2H_5)C_6H_{12}O]PO(OH)_2$,

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

symbolized as HDEHP, reported by two of us,[1] it was noted that the distribution ratio, K, is third-power dependent upon the HDEHP concentration in the organic phase but that, in low-acidity systems, a solid phase appears when the ratio of M^{+3} to DEHP anionic entity exceeds 1 : 6. It was suggested[1] that these data are consistent with the assumption of a dimeric anionic entity, $[H(DEHP)_2]^-$.

In a similar study involving the corresponding mono-ester, $[(C_2H_5)C_6H_{12}O]PO(OH)_2$, symbolized as H_2MEHP, it has now been noted that the dependence of K upon solvent concentration is a function of the method of solvent preparation and may be made to vary over a wide range.

From the well-established polymerization tendencies of inorganic phosphates, it seemed logical to explain the foregoing HDEHP and H_2MEHP data respectively in terms of dimerization and extensive polymerization of the free acid. Accordingly, molecular weight determinations of carefully purified samples of these acids and several other organic phosphorus compounds were made by the freezing-point depression method, using benzene as the cryoscopic medium.

Regardless of the method of preparation, all samples of HDEHP proved to be dimeric. Samples of H_2MEHP, formula weight 210·2 g, of average molecular weight ranging from 1500 g to 2500 g have been studied.

The corresponding di- and mono-*n*-butyl esters, symbolized as HDBP and H_2MBP, have been found to be respectively dimeric and extensively polymeric. Likewise, the di- and mono-*n*-octyl esters, symbolized as HDOP and H_2MOP, have been proved dimeric and extensively polymeric, respectively.

Under the same conditions, the neutral esters, tri-*n*-butyl orthophosphate, tri(2-ethyl hexyl) orthophosphate, tri(2-ethyl hexyl) phosphite, tri-*n*-butyl phosphite, and di-*n*-butyl *n*-butyl phosphonate have been found to be monomeric.

It is suggested that $[(RO)_2PO(OH)]_2$ may be represented as an eight-membered ring involving hydrogen bonding, the structure being analogous to that of an eight-membered ring carboxylic acid dimer,[2] and that the HDEHP extraction data for trivalent lanthanides and actinides may be explained on the basis of the ionization:

$$HDEHP_2 \rightleftharpoons H^+ + [H(DEHP)_2]^-$$

Similar hydrogen bonding may explain the molecular complexity of $(RO)PO(OH)_2$.

A detailed report of a more extensive study including the interactions between specific phosphorus compounds and water, thiocyanic acid, various mineral acids, and various metallic cations is being prepared. This report will include data on *cyclo*hexyl, benzyl, and aryl analogues of the alkyl compounds discussed above and will present methods of preparation and purification.

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[1] D. F. Peppard, G. W. Mason, J. L. Maier, and W. J. Driscoll *J. inorg. nucl. Chem.* **4**, 334 (1957).
[2] N. V. Sidgwick *Annual Reports* **30**, 114-115 (1934).

Multiple bonding in phosphorus compounds

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Van Wazer[1] has recently reviewed the experimental evidence for the partial double-bond character of bonds in which at least one partner is a phosphorus atom. Using a bond length and a thermochemical method, he obtained degrees of double-bond character with qualitative agreement between the two methods, although the quantitative results differed considerably. The most striking generalization apparent from the tabulation and stressed by Van Wazer is that, with few exceptions,

[1] J. R. Van Wazer *J. Amer. chem. Soc.* **78**, 5709 (1956).

tri-, penta-, and hexa-co-ordinated phosphorus forms essentially exclusively single bonds, while mono- and tetra-co-ordinated phosphorus almost invariably gives rise to bonds of appreciable multiple-bond character.

This generalization can readily be understood from a consideration of the overlap integrals associated with the potential π bonds. First, assume that the single-bond skeleton in the compounds considered provides the major portion of the total binding energy, and almost completely determines the geometry of the molecule. This assumption appears perfectly reasonable, at least in all cases where multiple-bond character is liable to be relatively small. Then, consider the multiple-bond formation as superimposed on this single-bond skeleton. In tri-co-ordinated compounds, the phosphorus atom of the single-bond skeleton is neutral, and accordingly the effective nuclear charge (Z_{eff}) calculated by SLATERS recipe for a $3d\pi$ orbital is zero and leads to a vanishing overlap integral (S) with a π orbital of a ligand atom or group.[2] If the ligands are *substantially* more electronegative than phosphorus (e.g. fluorine), considerable charge is inductively withdrawn from P, leading to a partially positive P atom, to non-vanishing values of Z_{eff} and of S.[3] This argument shows that, in agreement with experimental findings, one would expect multiple bonds in tri-co-ordinated P only in compounds with *strongly* electronegative ligands.

The single-bond skeleton of tetra-co-ordinated phosphorus compounds leaves the P atom with a formal positive charge. Consequently Z_{eff} for a $3d\pi$ orbital, and S for its overlap with a ligand π orbital do not vanish, and multiple-bond formation follows. Since the charge on the P atom increases with the electronegativity of the ligands, the multiple-bond character should increase in the same way. The accuracy of the data cited by VAN WAZER does not permit a test of this argument. In one particularly favourable case, however, the argument appears well substantiated; PF_3 forms stronger double bonds than PCl_3 or $P(CH_3)_3$ with Pt in the complexes of Pt^{++}.[4]

In the case of penta- and hexa-co-ordinated compounds, the single-bond skeleton again leaves the central atom neutral or negatively charged, and vanishing Z_{eff} and S lead to negligible multiple bonding. With the most electronegative ligand (F) in PF_5 and PF_2Cl_3, again sufficient charge is inductively withdrawn from the P atom to lead to some π bonding.

Monocovalent phosphorus of course has p electrons available, and in the compounds cited by VAN WAZER as involving π bonds (P_2, PN, PO, PC) we undoubtedly deal with simple π bonds involving exclusively, or almost exclusively, the $p\pi$ orbitals. Similar π bonding (conjugation) can also be demonstrated for tricovalent phosphorus when one or more of the ligands are unsaturated organic radicals.[5]

The types of argument presented here can, of course equally well be applied to compounds of other second-row elements. Unfortunately, no such extensive tabulations as VAN WAZER'S exist for other elements.

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[2] H. H. JAFFÉ *J. chem. Phys.* **21**, 258 (1953).
[3] H. H. JAFFÉ *J. phys. Chem.* **58**, 185 (1954).
[4] J. CHATT and A. A. WILLIAMS *J. chem. Soc.* 3061 (1951); J. CHATT and R. G. WILKINS *Ibid.* 273 (1952).
[5] H. H. JAFFÉ *J. chem. Phys.* **28**, 1430 (1954).

A new preparation of magnesium *cyclo*pentadienide

(*Received* 10 *December* 1956)

IT HAS been known for many years[1] that alkali metals react with *cyclo*pentadiene at room temperature, liberating hydrogen and forming the alkali salt MC_5H_5. Apart from these metals, however, only iron has been reported to react directly with the hydrocarbon, forming the "sandwich type" compound

[1] J. THIELE *Ber.* **34**, 68 (1901).

ferrocene.[2] This reaction takes place at 200–300°C, but proceeds for only a short time, after which the iron no longer reacts. The purpose of the present note is to report a smooth, continuous, direct reaction of magnesium metal with *cyclo*pentadiene at 500–600°C forming magnesium *cyclo*pentadienide $Mg(C_5H_5)_2$. Previously this compound had been prepared only by the thermal decomposition of the *cyclo*pentadienyl Grignard reagent.[3,4]

Carefully excluding air and moisture, and using an inert carrier gas (e.g. helium, argon, etc.), freshly prepared *cyclo*pentadiene vapour was passed over magnesium metal powder in a porcelain boat at 500–600°C. A reaction started immediately and proceeded smoothly as long as the *cyclo*pentadiene flow was continued. Colourless crystals of $Mg(C_5H_5)_2$ deposited on the cooler surfaces at the exit end of the furnace. These crystals were well developed if the deposition was very slow, but generally the deposit was a white polycrystalline mass of fine dendritic crystals. These small crystals decomposed extremely rapidly on exposure to moisture or oxygen. Well developed crystals with a melting point of 176°C could be obtained by slow sublimation.

It is interesting to note that the cracking of straight-chain aliphatic hydrocarbons over magnesium metal at about 700°C also produces small quantities of magnesium *cyclo*pentadienide $Mg(C_5H_5)_2$. This phenomenon was observed with *n*-butane, pentane (mixture of normal and *iso* isomers), *n*-hexane, and *n*-heptane, but only to a limited extent with propane. On the other hand, no $Mg(C_5H_5)_2$ was formed in the cracking of pure *iso*butane or *neo*pentane over magnesium metal. Further experiments of this type would give information about the cyclization processes taking place during hydrocarbon cracking.

The author wishes to acknowledge the assistance of Mr. L. A. PAPAZIAN in carrying out some of these reactions.

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[2] T. J. KEALY and P. L. PAUSON *Nature, Lond.* **168**, 1039 (1951).
[3] G. WILKINSON and F. A. COTTON *Chem. and Ind. (Rev.)* 307 (1954).
[4] G. WILKINSON, F. A. COTTON, and J. M. BIRMINGHAM *J. inorg. nucl. Chem.* **2**, 95 (1956).

The intermediate in the preparation of perchloryl fluoride

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A. A. WOOLF has commented[1] on the intermediate in the preparation of perchloryl fluoride, referring to our previous publication.[2] Dr. WOOLF mistakenly inferred that $(ClO_2)_2S_2O_{10}$ was considered by us to be an intermediate in the formation of perchloryl fluoride. The colour-changes as well as the formation of chlorine, oxygen, and sulphur trioxide described in our publication[2] are quite distinct from the mechanism for the formation of perchloryl fluoride. We believe, along with WOOLF, that the acid-base mechanism is important in the formation of perchloryl fluoride.

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[1] A. A. WOOLF *J. inorg. nucl. Chem.* **3**, 250 (1956).
[2] G. BARTH-WEHRENALP *J. inorg. nucl. Chem.* **2**, 266 (1956).

Hydration of uranyl nitrate in organic solvents

(*Received* 15 *March* 1957)

KATZIN[1] has recently discussed the solution of inorganic salts in organic solvents. In the course of his paper he states that, under conditions of equilibrium with an aqueous phase, each uranyl nitrate molecule in *iso*butyl alcohol, diethyl ether, or methyl *iso*butyl ketone is accompanied by 4·0 molecules of water. He concludes that a species $[UO_2(NO_3)_2(H_2O)_4]$ is formed, in which the waters are not easy to replace with organic solvent molecules. In diethyl cellosolve (ethylene glycol diethyl ether), the figure for water molecules per uranyl nitrate is said to be 6·0—which is ascribed to electrostatically associated $[UO_2(H_2O)_6](NO_3)_2$—changing abruptly to 4·0 as the uranyl nitrate concentration increases. All these results are quoted from an earlier paper by KATZIN and SULLIVAN.[2]

MATHIESON and MCKAY[3] have also studied these systems, as well as a number of similar ones. Except in the case of *iso*butyl alcohol, their results fall tolerably close to KATZIN and SULLIVAN's. However in some cases at least they made a more detailed examination of the shapes of the water content curves, and the results as a whole leave little doubt that KATZIN and SULLIVAN's conclusions are oversimplified. The number of waters per uranyl nitrate molecule often approximates to 4·0, it is true, but not in all cases; moreover, it is quite common for the number to fall gradually (not abruptly) as the uranyl nitrate concentration increases.[4] In alcoholic solvents, including *iso*butyl alcohol, quite complicated curves were observed when water content was plotted against uranyl nitrate concentration, and no single water : uranyl nitrate ratio could be distinguished.

Now KATZIN's argument requires that the tetrahydrate be formed in partition equilibria to the virtual exclusion of other hydrates; for otherwise there is no clear link between the 4 : 1 ratio for water : uranyl nitrate and the formula of the tetrahydrate. MCKAY and MATHIESON's observations tend to undermine the argument by showing that the 4 : 1 ratio is less definite than KATZIN supposes.

In view of the doubts, GARDNER, MCKAY, and WARREN[5] have attacked the problem from another angle. They studied how the water content of solutions of uranyl nitrate in two organic solvents depended on the water-vapour pressure. The curves obtained might be expected to show some kind of a step in the water-content curve at a composition corresponding to the tetrahydrate. However, the only indication of a step was at very low water-vapour pressures, corresponding to a dihydrate. Thereafter the water-content curve rose steadily with no sign of flattening out; higher water contents than would correspond to a tetrahydrate were ultimately reached.

If GARDNER, MCKAY, and WARREN's results are to be explained in terms of hydrates, then it must be a whole series of hydrates, ranging at least from the di- to the hexa-hydrate, in equilibrium with one another, and of comparable stability. But the water : uranyl nitrate ratio of 4 : 1 then becomes a mean hydration number and loses all force as an argument for the existence of a tetrahydrate; the fact that it happens to be more or less integral can only be regarded as fortuitous. We must evidently be very cautious in drawing conclusions from the water content of the organic phase in a partition equilibrium. This applies, of course, not only to uranyl nitrate systems but to all those considered by KATZIN, e.g. those containing thorium nitrate.

KATZIN's point of view would be particularly difficult to maintain in relation to nitric acid partitions. The experiments[6] show that the number of water molecules accompanying each nitric acid molecule in different ethers is as follows:

Dibutyl ether	0·88
Dibutyl carbitol	1·82
Penta-ether	6·4

[1] L. I. KATZIN *J. inorg. nucl. Chem.* **4**, 187 (1957).
[2] L. I. KATZIN and J. C. SULLIVAN *J. phys. Chem.* **55**, 346 (1951).
[3] H. A. C. MCKAY and A. R. MATHIESON *Trans. Faraday Soc.* **47**, 428 (1951).
[4] See also Fig. 4 of H. A. C. MCKAY *Chem. and Ind.* (*Rev.*) 1549 (1954).
[5] A. R. GARDNER, H. A. C. MCKAY, and D. T. WARREN *Trans. Faraday Soc.* **48**, 997 (1952).
[6] E. GLUECKAUF and H. A. C. MCKAY (unpublished).

It is, of course, possible that (say) mono-, di-, and hepta-hydrates are formed respectively in the three solvents, but this seems an improbable explanation.

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Radiometric titration of 10^{-7}–10^{-5} gram amounts of transition metals

(*Received* 4 *December* 1956)

ALTHOUGH isotope dilution and radioactivation techniques have been widely investigated, it is only very recently that radiometric methods have been studied in detail. MOELLER *et al.*[1] have reported the estimation of chloride using radioactive Ag^+, and of sulphate using radioactive SO_4^{2-}. ALIMARIN[2] has described the estimation of magnesium with $^{32}PO_4^{3-}$, and cobalt with $^{60}Co^{2+}$, using ferrocyanide. In this work, precipitation reactions were used, the end-point being determined by the appearance of activity in the aqueous phase, or its disappearance from the aqueous phase, according to circumstances. The sensitivity was limited to milligram amounts, necessary for handling precipitates. If, however, solvent extraction methods are chosen, the limits of sensitivity are determined primarily by the impurity level. It is the purpose of this note to point out that the radiometric method, when applied to suitable systems (of which there are a large number), is capable of high sensitivity and accuracy. As a particular example we have investigated the use of dithizone in chelometric titrations of transition metal ions. Two techniques have been used.

ISOTOPIC TRACER

The radioactive indicator was an isotope of the element being estimated. A 2×10^{-5} to 5×10^{-5} M carbon tetrachloride solution of dithizone was titrated from a burette into a vessel containing 6·5 to 10 ml of an aqueous solution of the salt of the metal ion (adjusted to the correct pH), the mixture being shaken until complete reaction had occurred. Aliquots (5 ml) of the aqueous solution were measured for activity in a liquid Geiger-Müller counter after each addition of dithizone solution. All reagents were carefully purified by conventional methods.[3] The concentration of dithizone was determined by titration with standard silver nitrate, and checked by measuring the extinction coefficient at a wavelength of 620 mμ. The two methods agreed within 0·5%. Before use, the glassware was washed with doubly-distilled water, then with a carbon tetrachloride solution of dithizone, dried, and waterproofed by treatment with "Desicote" to minimize exchange of metal ions between the glassware and the solutions. A "Desicoted" surface repels water, and allows complete draining of the Geiger-Müller counter when the 5-ml aliquots are returned to the original titrating vessel.

Typical titration curves are shown in Fig. 1, and some results are given in Table 1. With the specific activity available (16·2 μc/μmole for ^{60}Co) a change in counting rate of about 300 counts/min was observed with cobalt on the 0·1 γ level (1 $\gamma = 10^{-6}$ g). In spite of the precautions taken, impurities in the reagents and on the vessel walls began to become significant at this level. Otherwise there would have been no great difficulty in estimating 0·01 γ of cobalt using more sensitive methods of measuring the activity. Since carrier-free material would in principle allow a sensitivity better by several powers of 10, the method is limited only by the degree to which other metals, extractable under the same conditions, can be removed. Elements which are not extracted until higher pH's do not interfere, and those which react at 2 or more pH units below the element being assayed are

[1] D. W. MOELLER, J. G. TERRILL, and M. S. SEAL *Proceedings of International Conference on the Peaceful Uses of Atomic Energy, Geneva* P/233. Vol. 15. p. 49 (1956).
[2] I. P. ALIMARIN *Ibid.* P/706, 60 (1956).
[3] WELCHER *Organic Analytical Reagents* Vol. 3. p. 463. Van Nostrand (1948).

quantitatively removed before it commences to react, provided they are not present in greater than tenfold excess. For instance, cobalt can be determined at the 1 γ level in the presence of similar amounts of Cd, Zn, Cu, Ni, Mn, Ag, Hg, etc., using dithizone. All the extractive titrations of cobalt with dithizone, using the conditions described above, gave a cobalt-to-dithizone ratio of 1 : 3,[4] in contrast to previously reported values of 1 : 2.[5,6] Oxidation of covalently bound cobalt often takes place in the presence of air. Under the conditions of this titration, a cobalt : dithizone ratio of 1 : 3 was always obtained (seventy determinations). A full report of the physical chemistry of this system is in preparation.[4]

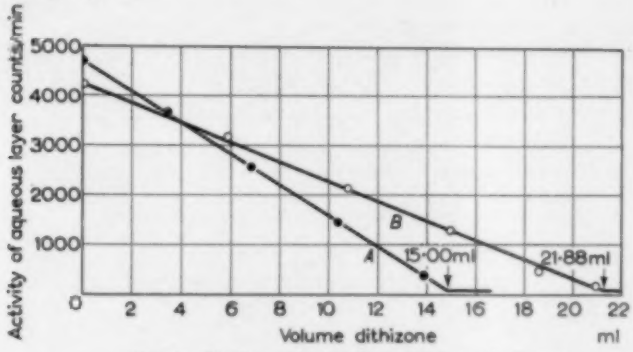

FIG. 1.—Radiometric titrations with isotopic tracers.

Curve *A*: cobalt (^{60}Co). Curve *B*: mercury (^{203}Hg). Ordinates; counts/min of a 5 ml liquid sample for cobalt. 5-min count of a dried $\frac{1}{4}$ ml aliquot for mercury. Abscissa; ml of dithizone solution. $3{\cdot}62 \times 10^{-5}$ M for cobalt. $1{\cdot}84 \times 10^{-6}$ M for mercury.

	Co^{2+}	Hg^{2+}
Added	$10{\cdot}7_8\,\gamma$	$40{\cdot}0\,\gamma$
Found	$10{\cdot}6_7\,\gamma$	$40{\cdot}1\,\gamma$

TABLE 1.—ISOTOPIC TRACER

Assayed element	Radio-tracer	Buffer	pH	Amount added (γ)	Amount estimated (γ)	Number of determi-nations
Mercury as nitrate	^{203}Hg	0·1 N HNO_3	~1·0	40·0	40·1	1
(in presence of 6 γ Cu^{2+})	^{203}Hg	0·1 N HNO_3	~1·0	$4{\cdot}0_0$	$4{\cdot}2_1$	1
Cobalt as nitrate	^{60}Co	Acetate	6·5–6·8	$10{\cdot}1_5$	$10{\cdot}2_0 \pm 0{\cdot}05$	8
Cobalt as nitrate	^{60}Co	Acetate	6·7	$3{\cdot}6_0$	$3{\cdot}6_7 \pm 0{\cdot}09$	2
Cobalt as nitrate	^{60}Co	Acetate	6·7–7·3	$2{\cdot}0_0$	$2{\cdot}0_3 \pm 0{\cdot}04$	6
Cobalt as nitrate	^{60}Co	Acetate	6·7	$1{\cdot}0_0$	$1{\cdot}0_6 \pm 0{\cdot}02$	4
Cobalt as nitrate	^{60}Co	Acetate	6·7	$0{\cdot}2_0$	$0{\cdot}27 \pm 0{\cdot}02$	3

[4] J. F. DUNCAN and F. G. THOMAS, to be published.
[5] A. T. PILIPENKO *Zh. Anal. Khim.* **8**, 286 (1953).
[6] S. MIYAKAWA and T. UEMURA *Bull. chem. Soc. Japan* **24**, 25 (1951).

NON-ISOTOPIC TRACER

In this method, extraction of the element to be assayed is followed by means of a radioactive tracer of an element which is extracted at a similar, but slightly higher, pH, and which does not enter the organic phase until reaction of the element being assayed is complete. Zinc may be determined in the presence of cobalt—and the latter may also be assayed in the same titration. Fig. 2 shows an experiment in which 6·9$_0$ γ of zinc and 10·1$_8$ γ of cobalt (tagged with ^{60}Co tracer) were titrated with 4·42 × 10^{-5} M dithizone solution, the aqueous solution being at pH 6·9. The initial flat portion of the titration curve corresponds to the extraction of zinc, and the sloping part to the extraction of cobalt. The estimated amounts were 6·8$_9$ γ of zinc and 10·2$_7$ γ of cobalt. At this level no interference from impurities was noticed. Some typical results are given in Table 2.

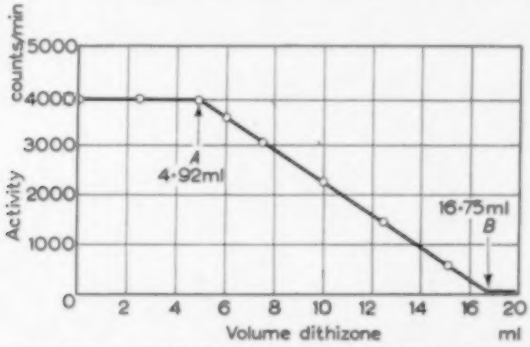

FIG. 2.—Radiometric titration of cobalt and zinc using Co^{60} tracer. Point *A* corresponds to the titre for zinc, point *B* to the titre for zinc and cobalt together.

	Co^{2+}	Zn^{2+}
Added	10·1$_8$$\gamma$	6·9$_0$$\gamma$
Found	10·2$_7$$\gamma$	6·8$_9$$\gamma$

TABLE 2.—NON-ISOTOPIC TRACER ANALYSIS OF ZINC AND COBALT (AS NITRATES) USING ^{60}Co
Buffer: sodium acetate-acetic acid

pH	Zinc added (γ)	Cobalt added (γ)	Zinc found (γ)	Cobalt found (γ)
5·7	6·9$_0$	10·1$_8$	7·1$_0$ ± 0·0$_3$	10·7$_7$ ± 0·0$_3$*
6·9	6·9$_0$	10·1$_8$	6·8$_9$ ± 0·0$_2$	10·2$_7$ ± 0·0$_3$
6·7	6·9$_0$	2·0$_0$	6·8$_9$ ± 0·0$_2$	2·1$_0$ ± 0·0$_4$
6·7	0·69$_0$	2·0$_0$	0·70 ± 0·02	1·9$_8$ ± 0·0$_3$
6·6	0·34$_5$	2·0$_0$	0·40 ± 0·01	2·0$_1$ ± 0·0$_3$

*The reaction with cobalt is so slow at this pH that it is doubtful if equilibrium had been reached at the last two points of the titration curve, even after shaking for at least 10 min.

CONCLUSIONS

Owing to the interference from impurities in these methods, activation analysis is, in practice, usually more sensitive. But the following aspects are worth noting:

(1) A reactor is not required at the site of the experiment—which is a real advantage in some countries.

(2) Sensitivity is, in principle, as great as in activation analysis, since in both the ultimate controlling feature is the specific activity available.

(3) The principles on which this method is based are general, so that the same type of method may be used for any analysis desired, either on the macro, or on the ultra-micro scale.

(4) The method as described above gives a sensitivity for cobalt (0·2 γ) and zinc (0·4 γ) which is comparable with the most sensitive of colorimetric methods but is more sensitive, by about a factor of 10, than conventional extractive titration procedures. Higher precision is also obtained.

Acknowledgements—One of us (F. G. T.) acknowledges the support of a Graduate Research Studentship from the Australian Atomic Energy Commission. This department (Prof. J. S. ANDERSON) is also supported by a research contract from the A.A.E.C., for which thanks is due.

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Radiometric titration with silver and cobalt tungstates

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THE composition of tungstate solutions at different pH has still not been adequately investigated. This note reports some new facts germane to this problem. A radiometric method was used, in which labelled silver nitrate (Ag^{110}) or cobalt nitrate (Co^{60}) was titrated from a burette into a solution of

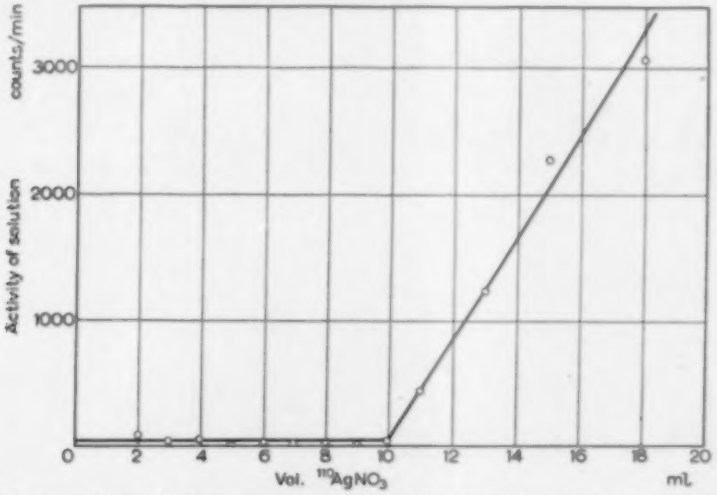

FIG. 1.—Radiometric titration of 10 ml 0·1 N sodium tungstate, with 0·1 N silver (Ag^{110}) nitrate. Unbuffered, pH 6·2–7·8.

sodium tungstate adjusted to the desired pH. Fig. 1 shows a typical titration curve with silver, from which it will be seen that the end point, and hence the Ag : W ratio, is easily calculated. The following results were obtained.

Metal : tungstate ratio

Precipitation of cobalt tungstate occurred only at pH > 6·5, whereas silver tungstate was still being precipitated at pH = 3·5. The cobalt tungstate was analysed by the non-isotopic tracer method —that is, the cobalt content of the solid was estimated from the measured activity of a known weight

and found to give 23·5 ± 1·5% cobalt, compared with 19·3% for $CoWO_4$, and 11·0 for $Co_3W_6O_{21}$. On the other hand, the silver tungstate composition varied with pH (Fig. 2). This we ascribe to precipitation of $Ag_6W_6O_{21}$ at low pH, whereas the corresponding cobalt paratungstate tungstate is apparently soluble, perhaps due to heteropoly acid formation (BAKER and MCCRUTCHEON[1]).

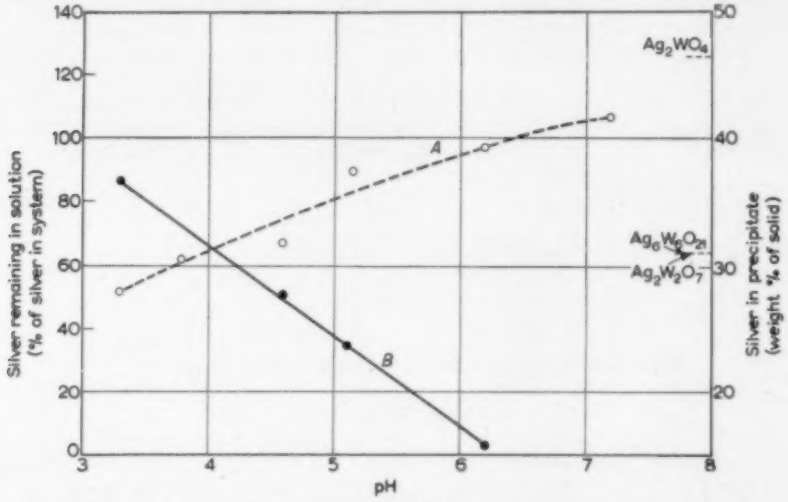

FIG. 2.—*A*: Variation of Ag : W ratio in precipitate. *B*: Per cent Ag remaining in solution at different pH.

Rate of reaction

The analysis for $CoWO_4$ reported above was made on a specimen which was precipitated in the cold. It was noticed, however, that, whereas precipitation of silver was immediate, precipitation of cobalt was sluggish (especially for pH < 8), and no sharp end-point could be obtained in the cold. Precipitation continued overnight. However, complete precipitation of cobalt tungstate occurs on boiling the solution, and a radiometric titration curve such as shown in Fig. 3 may be obtained. A Co : W ratio of 0·98 (estimated from the end-point) was obtained for pH > 8. The amount of cobalt tungstate precipitated in the cold and hot at different pH is shown in Fig. 4. Also on the

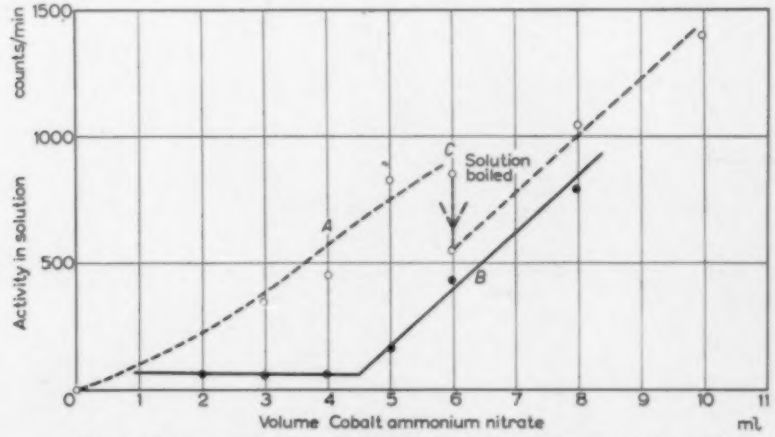

FIG. 3.—Radiometric titration of 10 ml 0·1 N sodium tungstate with 0·2 N cobalt (Co^{60}) ammonium nitrate. *A*: Points below *C* are at room temperature; others at boiling-point. *B*: Solution boiling throughout, pH 7·4.

[1] L. C. W. BAKER and T. P. MCCRUTCHEON *J. Amer. chem. Soc.* **78**, 4503 (1956).

same figure the diffusion coefficients measured by ANDERSON and SADDINGTON[2] are plotted. It will be seen that there is close correspondence, which suggests that the paratungstate ion plays an important role in preventing precipitation of cobalt tungstate.

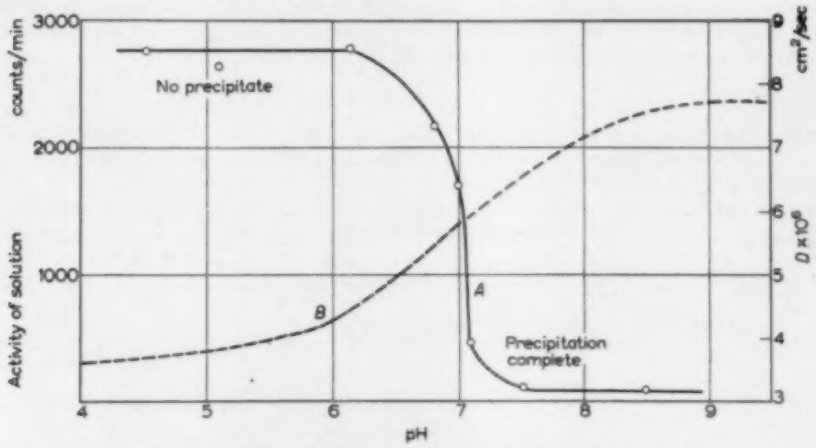

FIG. 4.—*A*: Amount of precipitated cobalt tungstate at different pH. *B*: Variation in diffusion coefficient of tungsten in tungstate solutions of different pH (after J. S. ANDERSON and K. SADDINGTON[2]).

Conclusions

From this work it would appear that:

(a) Precipitation of cobalt tungstate at high pH may be used to estimate the WO_4^{2-} content of tungstate solutions;

(b) The equilibrium between WO_4^{2-} and the paratungstate ion, or any complexes with cobalt, is not instantaneous.

(c) Conversion of condensed tungstate to WO_4^{2-} is complete at pH > 8.

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[2] J. S. ANDERSON and K. SADDINGTON *J. chem. Soc.* S381 (1949).

Paper chromatography of inorganic ions—XVI

A note on the paper chromatography of technetium using a long-life isotope

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PREVIOUS work on Tc in this laboratory[1,2] was carried out with the aim of obtaining a paper chromatographic separation of Tc from Re. At that time the only available isotope was Tc^{99} (5·9 hr) prepared by the laboratories of the Commissariat à l'Energie Atomique.

Since with many solvents a minimum of 18 hours is necessary for satisfactory development of a chromatogram, preliminary preparation of solutions and activity measurements after development had to be performed at considerable speed, and even then the chromatograms could only be run for 6–8 hours. Thus, although impurities were present in visible amounts in the Tc^{99} tracer, no preliminary purification was attempted.

[1] M. LEDERER *Analyt. chim. acta* 12, 146 (1955).
[2] R. G. de CARVALHO Paper read to the International Congress on Analytical Chemistry, Lisbon, September 1956.

We have recently been able to obtain 1 mg of the long half-life Tc^{99} ($2{\cdot}12 \times 10^6$ years) in the form of $KTcO_4$ (2·055 mg/ml) from Oak Ridge. It was decided to repeat the previous work as well as to extend it by examining others of the usual solvents used in inorganic paper chromatography. As shown in the experimental part below, all previous findings could be confirmed. In addition, the efficiency of the separations could be examined after overnight development. The best separation of Tc-Re so far obtained was with butanol-conc. HCl (1:1) as solvent.

EXPERIMENTAL

The ascending technique with sheets of Whatman No. 1 paper was used throughout. The radioactivity of the Tc^{99} was measured with an end-window counter for soft beta rays, each 5 mm being scanned along the paper.

Alkaline solvents. Table 1 shows the R_f values of the per-technetate and per-rhenate anions in various alkaline solvents used for the separation of anions. The R_f value differences previously observed[3] were again obtained; however, a comet extending forward from the spots was observed with the long-lived isotope, making separation in these solvents incomplete.

TABLE 1.—THE R_f VALUES OF PER-TECHNETATE AND PER-RHENATE IN VARIOUS SOLVENTS

Solvent	R_f values	
	Per-technetate	Per-rhenate
Butanol shaken with 1·5 N NH_4OH	0·375	0·42
*Iso*amyl alcohol shaken with 1·5 N NH_4OH	0·098	0·089
Butanol, pyridine, and 1·5 N NH_4OH (2 : 1 : 2) (for R_f values of other anions in this solvent see [3])	0·77	0·78
Butanol shaken with 10% acetic acid	0·30	0·32
Butanol shaken with 20% acetic acid	0·45	0·45
Butanol shaken with 30% acetic acid	0·49	0·53
Butanol-conc. HCl (1 : 1)	0·70	0·77
Butanol-conc. HCl (2 : 1)	0·78	0·78

Mixtures of butanol and acetic acid. Table 1 also gives the R_f values in butanol shaken with 10%, 20%, and 30% aqueous acetic acid. Very little, if any, separation effect is visible; however, both MoO_4^{--} and WO_4^{--} have been examined in butanol shaken with 10% acetic acid and remain at $R_f = 0$. Thus it should be possible to separate Re from irradiated W, and Tc from irradiated Mo, with this solvent. CNS^- moves in this solvent with an $R_f = 0{\cdot}395$ and is thus partially separated from ReO_4^-.

Mixtures of butanol and mineral acids. We examined various concentrations of HBr in butanol (0·1 N, 0·3 N and 1 N HBr) with the hope of obtained a lower valency of one or both elements; however, both TcO_4^- and ReO_4^- move consistently with the water front of the solvent, as in the case of mixtures of dilute HCl with butanol. Only the mixture butanol-conc. HCl (1 : 1) gave a satisfactory R_f difference as well as small round spots. An increase in the HCl concentration of the solvent makes the paper too fragile. A decrease (butanol : conc. HCl = 2 : 1) decreases the separation effect. According to the results of GERLIT[4] with solvent extraction, this separation in high concentrations of HCl is due to a reduction of the Tc(VII).

Some electrophoretic experiments. Using a simple paper electrophoresis apparatus, in which the paper is held between two glass plates,[5] we examined the movement of TcO_4^- and ReO_4^- with HCl, HBr, and HNO_3 as electrolytes. No separations were noted; both ions move with the same speed towards the anode.

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[3] F. H. POLLARD, J. F. W. MCOMIE, and I. I. M. ELBEIH *J. Chem. Soc.* 470 (1951).
[4] J. B. GERLIT *Peaceful Uses of Atomic Energy, Geneva* P/671. Vol. 7. (1955).
[5] M. LEDERER and F. L. WARD *Analyt. chim. acta* **6**, 355 (1952).

Alpha decay in plutonium-237*

(*Received* 19 *March* 1957)

^{237}Pu has been produced by JAMES and co-workers[1,2] by helium ion bombardment of ^{235}U and by deuteron bombardment of ^{237}Np. These investigators reported the half-life to be about 40 days and that the nuclide probably decayed by electron capture. The electron capture mode of decay was later confirmed by HOFF.[3] However, the existence of an alpha branch was not established. Therefore, with the availability of stronger sources of ^{237}Pu and equipment for alpha pulse analysis, it seemed worthwhile to re-examine the alpha spectrum of plutonium produced in bombardments of ^{235}U with helium ions in an attempt to detect any previously unidentified alpha groups which could be assigned to ^{237}Pu.

TABLE 1.—SUMMARY OF RATIOS FOR ^{237}Pu SAMPLES

Bombardment	$\frac{\Sigma\alpha \text{ (counts/min)}}{\Sigma\gamma \text{ (counts/min)}}$	$\frac{5{\cdot}34 \text{ MeV } \alpha}{\Sigma\alpha}$	$\frac{5{\cdot}34 \text{ MeV } \alpha \text{ decay}}{\text{electron capture decay}}$
I	$2{\cdot}00 \times 10^{-3}$	0·044	$2{\cdot}19 \times 10^{-5}$
II	$1{\cdot}87 \times 10^{-3}$	0·039	$1{\cdot}81 \times 10^{-5}$
			Average: $2{\cdot}0 \times 10^{-5}$

Two ^{237}Pu sources were produced, the first by a 2250 μAh bombardment of enriched ^{235}U foil with 26–29 MeV helium ions, and the second by 9280 μAh of ~30-MeV helium ions. After bombardment, the foils were dissolved in dilute HCl and the plutonium was isolated by cycles of reduced and oxidized fluorides and elutions[4] from anion resin columns with HI-HCl solution, which were continued until the ratio of alpha to gamma activity in the plutonium fraction remained constant.

TABLE 2.—HALF-LIFE OF ^{237}Pu

Sample	Decay period (days)	Half-life (days)	Standard deviation (days)
I	207	45·81	0·04
II	146	45·54	0·03
	Weighted average:	45·63	0·03
	Estimated error:	± 0·20	

In each case, the purified plutonium was diluted to known volume and standard aliquots were evaporated on 1-in-diameter platinum discs. For the determination of the alpha-to-gamma counting ratio (Table 1, column 2), these samples were alpha-counted in a 2π methane flow proportional counter (geometry = 52 ± 1 per cent), and thereafter were gamma-counted daily in standard geometry with a NaI(Tl) scintillation counter. Table 2 presents the values of the half-life obtained by a least-squares treatment of the scintillation counter data. The best value of the half-life is probably 45·63 days, with an estimated overall error of 0·20 days.

* This work was done under the auspices of the U.S. Atomic Energy Commission.

(1) R. A. JAMES, A. E. FLORIN, H. H. HOPKINS JR., and A. GHIORSO *The Transuranium Elements* Paper No. 22.8, National Nuclear Energy Series, Plutonium Project Record, Div. IV. Vol. 14B. Part II. p. 1604. Eds. G. T. SEABORG, J. J. KATZ, and W. M. MANNING. McGraw-Hill, New York (1951).
(2) R. A. JAMES, S. G. THOMPSON, and H. H. HOPKINS JR. *Ibid.* Paper 22.16. p. 1634.
(3) R. W. HOFF UCRL-2325, September (1953) (Unpublished).
(4) J-11 Collected Radiochemical Procedures (Radiochemistry Group J-11) LA-1721.

Alpha pulse analyses of aliquots of the ^{237}Pu solutions containing ~470 and ~2500 alpha counts/min, respectively, showed a previously unidentified alpha group at 5·34 ± 0·01 MeV. Fig. 1 shows the alpha spectrum of ^{237}Pu-II, an aliquot from the second bombardment. The alpha contribution from ^{237}Pu was obtained by subtraction of the alpha spectrum of the same sample taken after >90 per cent of the ^{237}Pu had decayed. There was also some evidence for another alpha group at 5·20–5·25 MeV in an abundance <20 per cent of the 5·34 MeV group. However, because of its position in the tail of the 5·34-MeV peak, absolute confirmation of this group was difficult. There was some indication of decay in the region from 5·60–5·65 MeV, but the tail from the 5·75 MeV peak

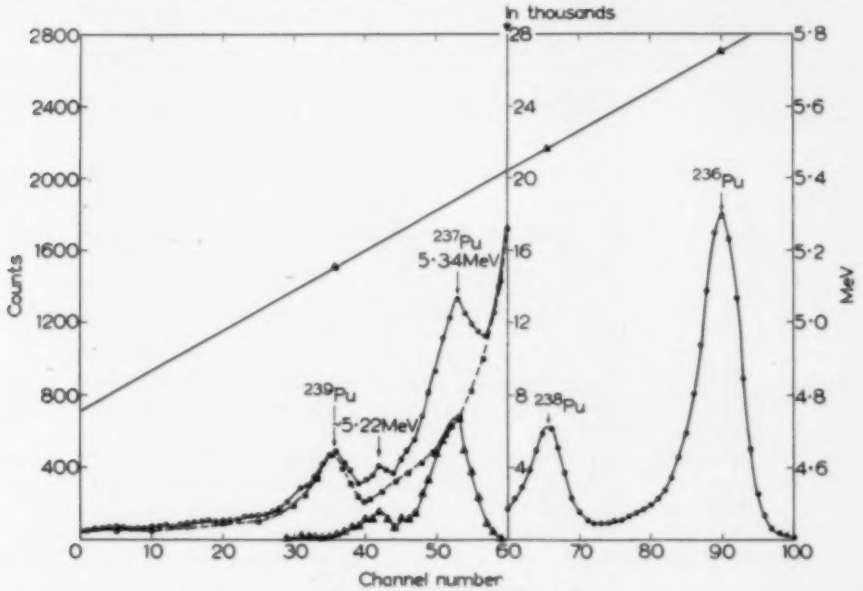


FIG. 1.—Alpha spectrum of sample of ^{237}Pu-II.
● 23 days after bombardment
■ 160 days after bombardment
▲ Alpha contribution from ^{237}Pu (by subtraction of later from earlier spectrum)

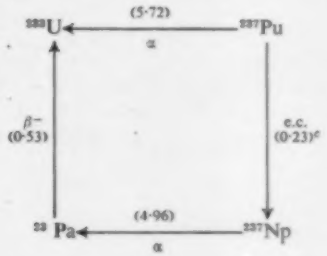
of ^{236}Pu precluded the detection of a low-abundance group in this region. However, an upper limit of ~ 25 per cent can probably be placed on such a component. Subsequent pulse analyses over a period of 5 months indicated that the first two alpha groups were decaying with a half-life of about 40 days. The half-life could not be accurately determined from alpha decay because of the large contribution to the alpha spectrum from ^{236}Pu, ^{238}Pu, and ^{239}Pu in the source. The ratio of the 5·34 MeV ^{237}Pu alpha activity to the total alpha activity (Table 1, column 3) was determined from several pulse analyses.

The major fraction (9·55 × 10^6 gamma counts/min) of the standardized ^{237}Pu solution from the first bombardment was analysed[5] for the alpha-emitter, ^{237}Np, 94 days after the last removal of neptunium from the plutonium. From the number of atoms of ^{237}Np in the solution, the electron capture disintegration rate of ^{237}Pu was calculated, and from this result the geometry-efficiency product of the scintillation counter was found to be 13 per cent for ^{237}Pu. From the geometries of the alpha and scintillation counters and the data in Table 1, the ratio of 5·34-MeV alpha decay to electron capture decay in ^{237}Pu was calculated to be 2·0 × 10^{-5}, with an estimated error of ± 0·4 × 10^{-5}. The ratio of total alpha decay to electron capture decay could be as much as 35 per cent higher if the other alpha groups are definitely assigned to ^{237}Pu.

According to the closed decay-energy cycle of GLASS, THOMPSON, and SEABORG[6] shown below,

[5] The author is indebted to Mrs. H. LOUISE SMITH for providing the ^{237}Np analysis.
[6] R. A. GLASS, S. G. THOMPSON, and G. T. SEABORG *J. inorg. nucl. Chem.* **1**, 3 (1955).

^{237}Pu was estimated to have an alpha decay energy of 5·72 MeV, which corresponds to a maximum alpha particle energy of 5·62 MeV. However, recent studies[7,8] show that the beta disintegration energy of ^{233}Pa is 0·568 MeV, and studies[9] at this laboratory indicate that 0·18 MeV is an absolute lower limit for the electron capture energy of ^{237}Pu. Hence the alpha decay energy predicted for ^{237}Pu is likely to be within 0·02 MeV of a lower limit, and the predominant mode of alpha decay in ^{237}Pu, which appears to be through the 5·34 MeV alpha group, must be to a level some 0·3 MeV above the ground state of ^{233}U.



In future studies an attempt will be made to utilize alpha-gamma coincidence measurements for the determination of the total alpha decay energy, and to prepare ^{237}Pu sufficiently free of ^{236}Pu to permit a more thorough investigation of possible higher-energy alpha transitions.*

It is a pleasure to acknowledge the co-operation of Dr. Donald Cochran and Dr. John Northrup in preparing the cyclotron targets, and of the Los Alamos cyclotron group in providing the bombardments. The author is also grateful to Mrs. Francine Lawrence for assistance with the chemistry and pulse analyses, to Dr. J. D. Knight for his valuable advice, and to Drs. C. I. Browne and G. A. Cowan for their continued interest in this work.

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* Subsequent to the preparation of this manuscript, R. Vandenbosch kindly transmitted to me a preprint of a paper by T. D. Thomas, R. Vandenbosch, R. A. Glass, and G. T. Seaborg, in which similar investigations of the alpha decay of ^{237}Pu are described. In general, our results appear to be in good agreement, and they were able to positively identify an alpha group at 5·65 ± 0·02 MeV in the decay of ^{237}Pu.

(7) W. D. Brodie *Proc. phys. Soc.* **A67**, 397 (1954).
(8) Ong Ping Hok and P. Kramer *Physica* **21**, 676 (1955).
(9) D. C. Hoffman, B. J. Dropesky *Electron Capture Decay of* ^{237}Pu (to be published).

SOME CURRENT PAPERS IN OTHER JOURNALS

Journal of Inorganic Chemistry, Volume 2, No. 1, 1957

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Gravimetric determination of palladium with 1,2-cyclohexanedionedioxime (nioxime). N. K. Pshenitsyn and O. M. Ivonina.

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Reviews and Bibliography

New treatise on inorganic chemistry. I. I. Vol'nov and P. Pascal.

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BOOK REVIEW

H. GERLACH: **Entwicklung und Gegenwärtiger Stand der Systematik der Transurane,** Berlin. Akademie-Verlag, 1955. ix + 256 pp., 29 D.M.

REMARKABLY little has so far been written with the object of giving the chemist a concise picture of the production and chemistry of the transuranic elements. The discursive volumes of the National Nuclear Energy Series are, in fact, almost the only major source of information apart from original papers and reports. This monograph is therefore of general interest, though it is intended primarily for German scientists, many of whom have had unusual difficulties in obtaining literature on the transuranics. The author introduces his subject with a brief account of the early work on nuclear reactions and then gives a detailed account of the various stages by which the true nature of nuclear fission came to be recognized. This historical survey is well done and is of considerable value, especially as there is a full bibliography.

The second part of the book is devoted to a description of the isotopes and general chemistry of the elements from neptunium to mendelevium. These are treated element by element, and in each case there is a detailed statement of the sequence of events leading to the discovery of the element. This is accompanied by a concise statement of their descriptive chemistry. The latter is accurate, though it is by no means complete, especially as regards the role of solvent extraction in separation processes. The author also includes very brief sections on the radioactive decay families, the electronic configurations of the transuranics and their place in the periodic table. The account of the $4n + 1$ series could well have been expanded considerably, and it would have been helpful to the general reader if the discussion of electronic configuration could have been more critical. This is especially important when a number of erroneous views on the electronic configuration are [illegible]. There is a long appendix in which are given tables of structural data for salts of the a[illegible] and redox potentials, together with lists of isotopes. The inclusion of various unusual for[illegible] of the periodic table seems rather out of place. These shortcomings do not, however, detract seriously from the usefulness of this book as a review of the field. The author has collected a great deal of widely scattered and not easily accessible information.

H. J. EMELEUS

ERRATUM

R. W. M. D'EYE and G. W. BOOTH: Further remarks on the hydrates of thorium tetrafluoride.

J. Inorg. Nucl. Chem. **4,** 13 (1957).

1st line p. 14 for $ThF_4.zH_2O$ read $ThF_4.xH_2O$

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